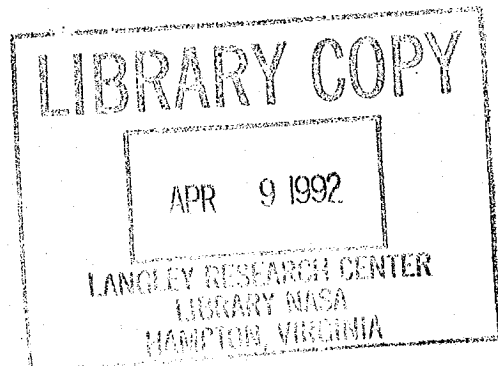NASA Technical Memorandum 105590

Glass Precursor Approach to High–Temperature Superconductors

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GLASS PRECURSOR APPROACH TO
HIGH-TEMPERATURE SUPERCONDUCTORS

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ABSTRACT

The available studies on the synthesis of high-T_c superconductors (HTS) via the glass precursor approach have been reviewed. Melts of the Bi-Sr-Ca-Cu-O system as well as those doped with oxides of some other elements (Pb, Al, V, Te, Nb, etc.) could be quenched into glasses which, on further heat treatments under appropriate conditions, crystallized into the superconducting phase(s). The nature of the HTS phase(s) formed depends on the annealing temperature, time, atmosphere and the cooling rate and also on the glass composition. Long term annealing was needed to obtain a large fraction of the 110 K phase. The high-T_c phase did not crystallize out directly from the glass matrix, but was preceded by the precipitation of other phases. The 110 K HTS was produced at high temperatures by reaction between the phases formed at lower temperatures resulting in multiphase material. The presence of a glass former such as B_2O_3 was necessary for the Y-Ba-Cu-O melt to form a glass on fast cooling. A discontinuous $YBa_2Cu_3O_{7-\delta}$ HTS phase crystallized out on heat treatment of this glass. Attempts to prepare Tl-Ba-Ca-Cu-O system in the glassy state were not successful.

1. INTRODUCTION

Interest in oxide ceramic superconductors was created with a breakthrough discovery of superconductivity at ~35 K in the $La_{2-x}Ba_xCuO_4$ system [1] which was soon followed by a superconducting transition temperature, T_c, of ~93 K in the Y-Ba-Cu-O system [2]. Superconductivity in the rare earth-free Bi-Sr-Cu-O system with a T_c of ~20 K was first reported by Michel et al [3]. The addition of calcium led to the discovery of bulk superconductivity at 85 K by Maeda et al [4]. Evidence for a superconducting phase with T_c of ~110 K in the

Bi-Sr-Ca-Cu-O system was presented soon after by Chu et al [5]. T_c in the $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ family increases with the number of Cu-O layers when n changes from 1 to 3. Phase pure superconducting materials for n = 1 and 2 have been synthesized by solid state reaction and other methods. However, preparation of a homogeneous single phase 110 K T_c material corresponding to n = 3 has been found to be much more tedious. So far, the highest confirmed T_c of 125 K has been reported [6] for the $Tl_2Ba_2Ca_2Cu_3O_x$ phase in the Tl-Ba-Ca-Cu-O system. Hereafter, phases will be denoted by their cation stoichiometry, e.g., 2212 for $Bi_2Sr_2Ca_1Cu_2O_8$.

The glass precursor technique as a preparative route for HTS is one of the most promising methods and offers several advantages. Mixing of the components occurs at molecular level in the melt. Almost fully dense, uniform, pore free materials can be fabricated and highly oriented grains can be achieved by crystallization under controlled conditions which could lead to high critical current densities (J_c). Heat treatments of the rapidly quenched glass can result in metastable crystalline phases having unusual properties which cannot be synthesized by normal means. True chemical homogeneity is possible as crystallization takes place from a homogeneous glass composition without the need for any long range diffusion. Microstructure of the product can be controlled by controlling the time and temperature of heat treatment. This method is also of practical significance for the manufacture of ceramic superconductors into desired shapes such as fibers, wires, tapes, etc. by borrowing the well-established techniques of glass technology.

There are also certain limitations of the melt quenching approach. The components should not be volatile at about one to two hundred degrees above the melting temperature. The melt must not phase separate and should not chemically react with the container. The last problem may, however, be alleviated through containerless melting [7].

The glass precursor method has been mostly applied for the synthesis of HTS in the Bi- system. However, some attempts have also been made in the Y-Ba-Cu-O and the Tl-Ba-Ca-Cu-O systems. A review of the glass precursor approach for fabrication of HTS is presented here.

2. GLASS SYNTHESIS

A flowchart of the process used for glass synthesis is shown in Fig. 1. The starting materials, usually metal oxides and carbonates, are mixed in appropriate amounts and loaded into a crucible (Pt, Ir, or Al_2O_3). The mixture is calcined at ~800-850 °C for carbonate decomposition and solid state reaction. The temperature is further raised to ~1000-1350 °C for melting and held for ~0.5 h for homogeneization. The melt is rapidly cooled by twin roller [8-14] quenching or by pressing between two metal plates resulting in black opaque glass. A typical x-ray diffraction pattern [15] of glass of $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ composition formed by quenching the melt between two copper plates is shown in Fig. 2. An amorphous halo alongwith some low intensity diffraction peaks, which can be assigned to CaO, are present indicating part of the CaO did not dissolve in the melt.
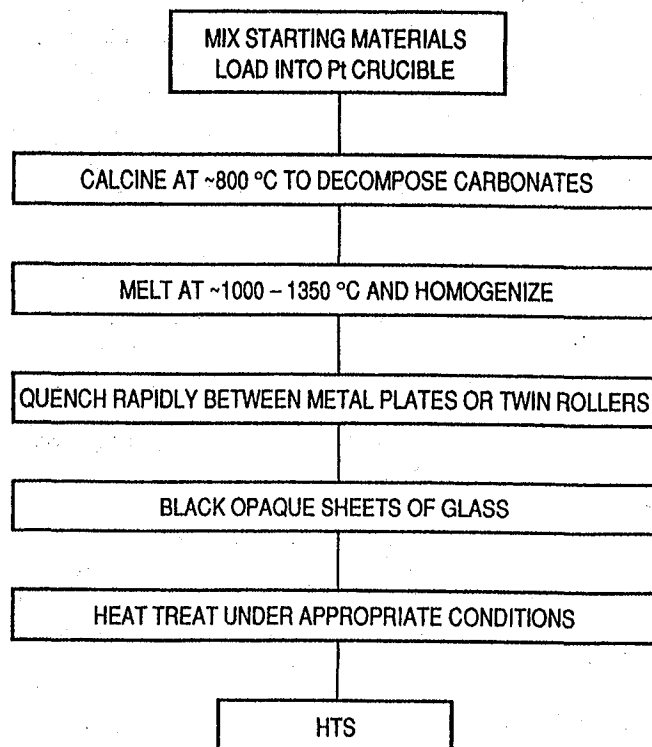
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                    ┌─────────────────────────┐
                    │   MIX STARTING MATERIALS │
                    │   LOAD INTO Pt CRUCIBLE  │
                    └─────────────────────────┘
                                 │
            ┌──────────────────────────────────────────┐
            │  CALCINE AT ~800 °C TO DECOMPOSE CARBONATES │
            └──────────────────────────────────────────┘
                                 │
            ┌──────────────────────────────────────────┐
            │   MELT AT ~1000 – 1350 °C AND HOMOGENIZE  │
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            │ QUENCH RAPIDLY BETWEEN METAL PLATES OR TWIN ROLLERS │
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            │  HEAT TREAT UNDER APPROPRIATE CONDITIONS  │
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                    │           HTS           │
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Fig. 1. A flow diagram showing the glass precursor approach for synthesis of high temperature superconductors.
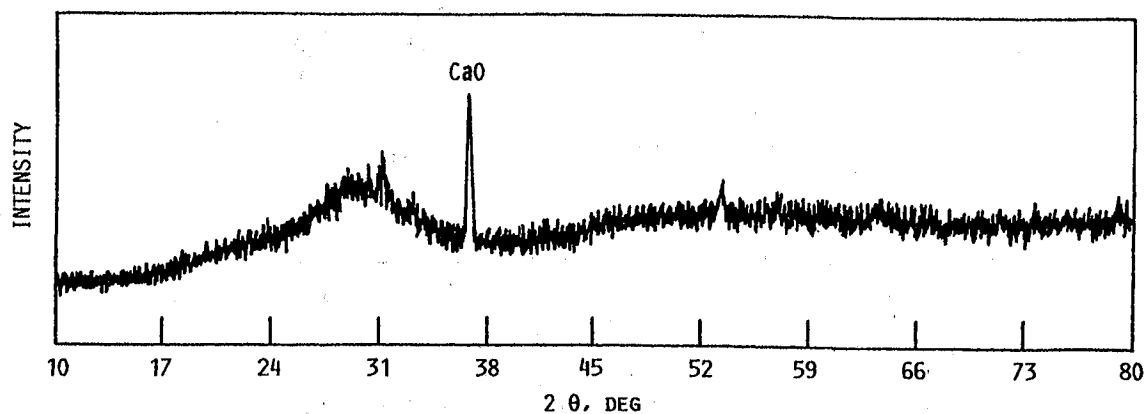
Fig. 2. Powder X-ray diffraction pattern of as-quenched glass of $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ composition. [15]

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A containerless [10-13] melting technique has also been used to avoid any contamination of the glass melt by corrosion of the crucible. In this method the constituent oxides are mixed in stoichiometric amounts, pressed into a bar, and sintered. The tip of the bar is melted using a flame or a thermal image furnace and the melt droplets are rapidly quenched by a metal twin-roller rotating at high speed. The details of this method are beyond the scope of this chapter but can be found elsewhere [10,16].

3. Bi-HTS SYSTEM

The glass precursor technique has been most widely used for the fabrication of HTS in the Bi-Sr-Ca-Cu-O [7-12,17-48] and the Pb-doped [13,15,49-62] systems as described below.

3.1. GLASS-FORMING REGIONS
3.1.1. Bi-Sr-Ca-Cu-O System

The glass forming region in the $BiO_{1.5}$-$(CaO.SrO)_{0.5}$-CuO system has been investigated [7] using a containerless glass melting technique. A relatively wide glass-forming region, as shown by the broken line in Fig. 3, exists in this pseudo-ternary system. This is quite interesting because no "network former" oxides are present in this system. The glass transition temperature, T_g (Fig. 4), was found to depend mainly on the $BiO_{1.5}$ content of the glass, with a maximum of 390°C at around 20 mol% $BiO_{1.5}$. The glasses of stoichiometric compositions such as $BiSrCaCu_2O_y$ and $Bi_2Sr_2Ca_2Cu_3O_y$ were also located in the region of the highest T_g.
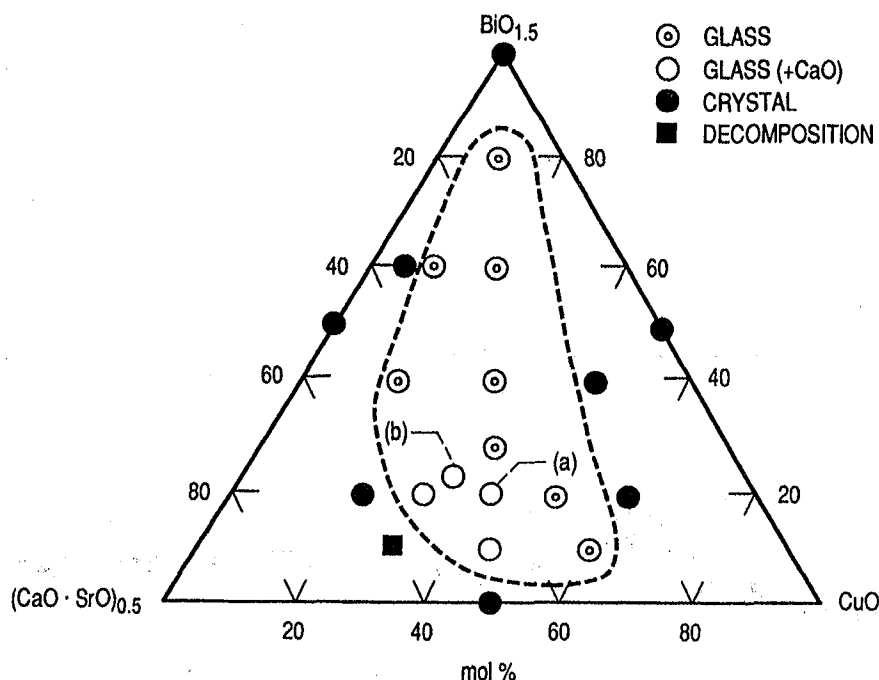
Fig. 3. Phase diagram showing glass forming region of the pseudo-ternary system $BiO_{1.5}$-$(SrO.CaO)_{0.5}$-CuO, SrO/CaO = 1; Compositions (a) and (b) correspond to $BiSrCaCu_2O_y$ and $Bi_2Sr_2Ca_2Cu_3O_y$, respectively. [7]

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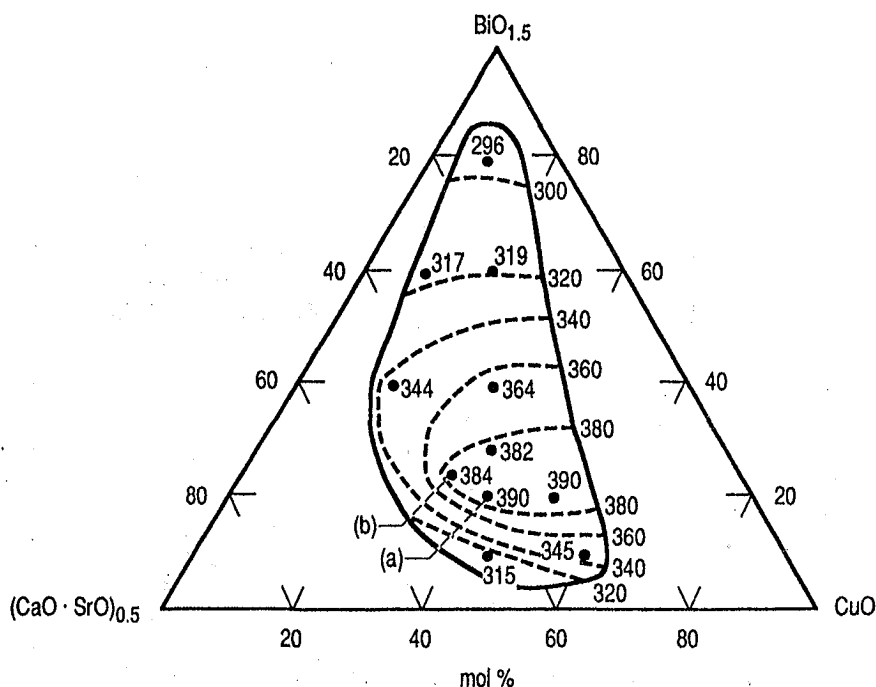
Fig. 4. Isotherms of glass transition temperature in the pseudo-ternary system $BiO_{1.5}$-$(SrO.CaO)_{0.5}$-CuO, SrO/CaO = 1; Compositions (a) and (b) correspond to $BiSrCaCu_2O_y$ and $Bi_2Sr_2Ca_2Cu_3O_y$, respectively. [7]

A typical DSC scan [18] of the $Bi_{1.5}SrCaCu_2O_y$ glass showing T_g and the crystallization temperature, T_x, is given in Fig. 5. Values of both T_g and T_x vary in a complex manner with increasing Bi_2O_3 content in the $Bi_xSrCaCu_2O_y$ glass as shown [26] in Fig. 6. Both T_g and T_x increase with the CaO content in the $Bi_{1.2}SrCa_zCu_2O_y$ glasses as shown [26] in Fig. 7. For Bi-Sr-Ca-Cu-O glasses, Zheng et al. [20] reported that values of T_g and T_x decrease with increase in CuO or Bi_2O_3 contents, and increase with increasing alkaline earth (CaO and SrO) content. The thermal stability factor [14] (T_x - T_g) is large for glasses rich in Bi_2O_3 and alkaline earth oxides whereas the CuO-rich glasses show smaller values. These results clearly indicate that Bi_2O_3 plays an important role in glass formation and also for thermal stability (T_x - T_g) of glasses in the Bi-Sr-Ca-Cu-O system. Results of Komatsu et al. [26] and Tohge et al. [7] also clearly indicate that Bi_2O_3 acts as a glass former and a decrease in Bi_2O_3 content degrades the glass-forming ability of the Bi-Sr-Ca-Cu-O system. This is reflected in Fig. 6 at Bi levels less than 1.5.

The effects of glass melting temperature and copper oxide content on the $Cu(I)/Cu_{total}$ ratio in the Bi-Sr-Ca-Cu-O glasses along with their T_g and T_x values are given [63] in Table I. Because of the reduction of copper oxide at high temperatures, most copper ions in these glasses quenched from high temperatures exist mainly in Cu(I) state. The $Cu(I)/Cu_{total}$ ratio increased with the glass melting temperature, but changed only negligibly with copper oxide content. However, the amount of Cu(I) in the glass, as indicated in the glass composition
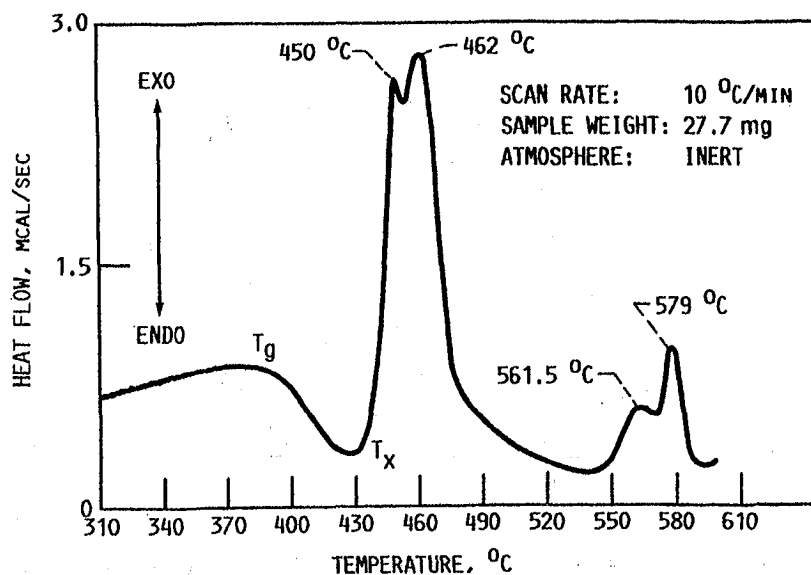
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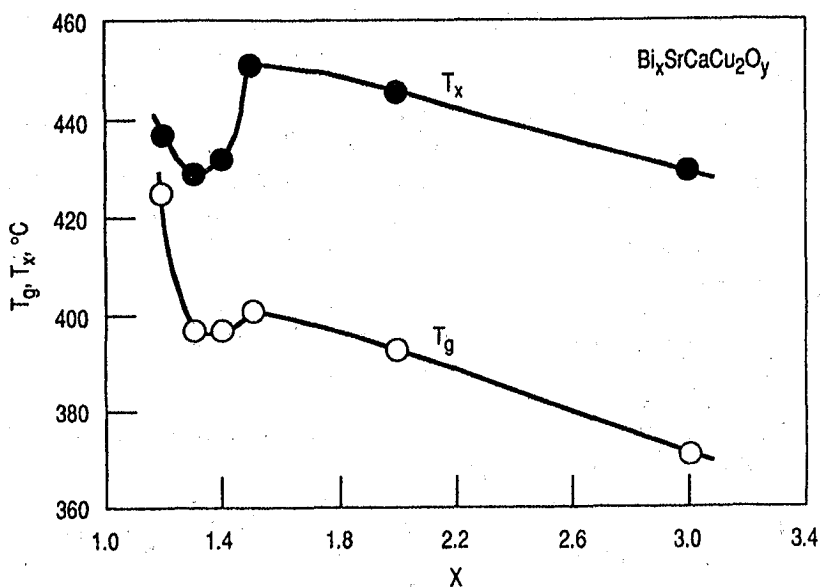Fig. 5. A typical DSC scan of $Bi_{1.5}SrCaCu_2O_y$ glass in inert atmosphere at a heating rate of $10^\circ C/min$. [18]

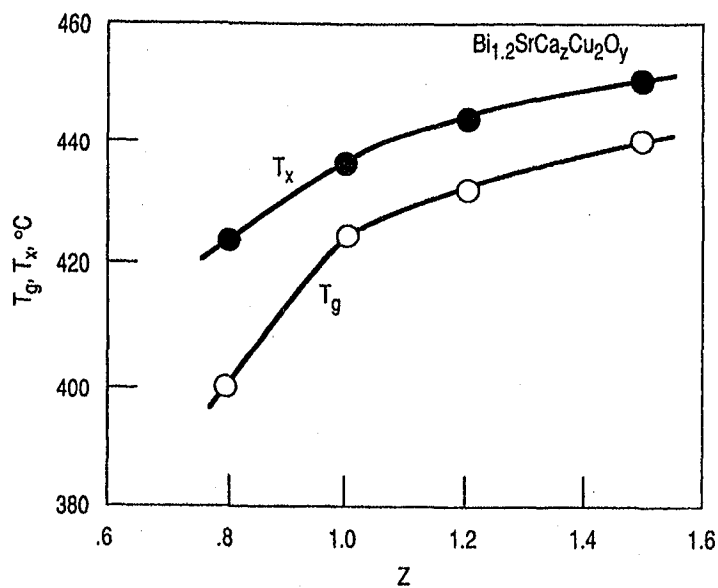Fig. 6. Effect of bismuth content on T_g and T_x for the $Bi_xSrCaCu_2O_y$ glasses. [26]

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Fig. 7. Influence of calcium content on T_g and T_x for the $Bi_{1.2}SrCa_zCu_2O_y$ glasses. [26]
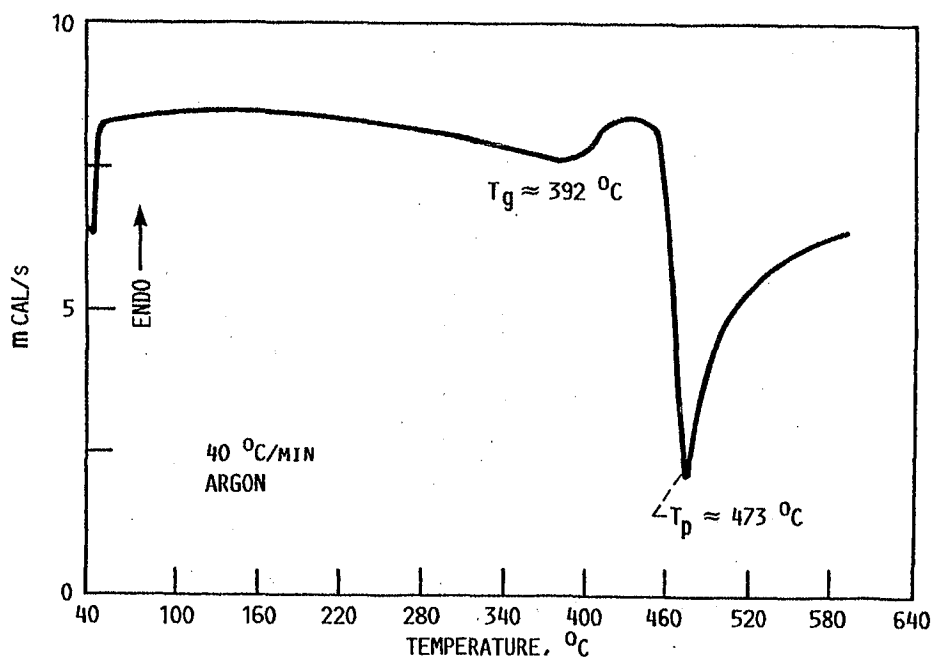
Fig. 8. A typical DSC scan of $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ glass recorded at a heating rate of 40°C/min in argon. [50]

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TABLE I. Effect of Glass Melting Conditions and Composition on Valence of Copper and Thermal Properties of Glasses in the Bi-Sr-Ca-Cu-O System [63]

Batch Composition	Melting Conditions[a]	$Cu(I)/Cu_{total}$	Mean Valence of Copper Ions in Glass	Resulting Glass Composition	T_g^{b} (K)	T_x^{b} (K)	T_x-T_g (K)
$Bi_4Sr_3Ca_3Cu_3O_y$	1050°C, air, 15 min	0.72	1.28	$Bi_4Sr_3Ca_3Cu(I)_{2.16}Cu(II)_{0.84}O_{13.92}$	695	768	73
$Bi_4Sr_3Ca_3Cu_4O_y$	1050°C, air, 15 min	0.66	1.34	$Bi_4Sr_3Ca_3Cu(I)_{2.64}Cu(II)_{1.36}O_{14.68}$	690	750	60
$Bi_4Sr_3Ca_3Cu_4O_y$	1200°C, air, 15 min	0.80	1.20	$Bi_4Sr_3Ca_3Cu(I)_{3.20}Cu(II)_{0.80}O_{14.40}$	689	745	56
$Bi_4Sr_3Ca_3Cu_4O_y$	1350°C, air, 15 min	0.85	1.15	$Bi_4Sr_3Ca_3Cu(I)_{3.40}Cu(II)_{0.60}O_{14.30}$	675	707	32
$Bi_4Sr_3Ca_3Cu_5O_y$	1050°C, air, 15 min	0.67	1.33	$Bi_4Sr_3Ca_3Cu(I)_{3.35}Cu(II)_{1.65}O_{15.33}$	686	743	57

[a] Pt crucible; Metal plate quench.

[b] DSC (10K/min) on bulk glass samples.

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TABLE II. Compositions, Glass Transition Temperature (T_g), Crystallization Temperature (T_x), and Thermal Stability (T_x-T_g) of Bi-Sr-Ca-Cu-O Glasses

Glass Composition	Glass Synthesis Method		T_g	T_x(onset)	T_x-T_g	Technique	Sample	Atmosphere	Ref.
	Melting	Quenching[a]	(K)	(K)	(K)	(10K/min)	Form		
$Bi_2Sr_2CuO_y$	-	A	679	709	30	DSC	-	Air	64
	1250°C, 10 min, Pt crucible	B	659	736	77	DTA	Bulk	Air	65
$Bi_2Sr_2CaCu_2O_y$	-	A	694	746	52	DSC	-	Air	64
	Air, Ir crucible	C	683	723	40	DTA	-	O_2	9
	Air, Ir crucible	C	683	723	40	DTA	-	N_2	9
$Bi_2Sr_2Ca_2Cu_3O_y$	-	A	688	734	46	DSC	-	Air	64
	Containerless	C	657	707	50	DTA	-	N_2 or air	13
	Air, Ir crucible	C	683	723	40	DTA	-	O_2	9
	Air, Ir crucible	C	683	723	40	DTA	-	N_2	9
	1150°C, 2h, Pt crucible	C	682	737	55	DTA	Powder	Air	14
	1170°C, 10min, Al_2O_3 crucible	B	670	738	68	DTA[c]	-	Air	66
$BiSrCaCu_2O_y$	Containerless	C	663	717	54	DTA	Powder	-	10
	1150°C, 2h, Pt crucible	C	703	739	36	DTA	Powder	Air	14
	Containerless	B	687	734[b]	47	DSC	-	-	29
$Bi_{1.5}SrCaCu_2O_y$	1300°C, 2h, Pt crucible	B	663	710	47	DSC	Bulk	Air	18
	Containerless	C	679	725	46	DSC[d]	Bulk	He	11,12
	Containerless	C	656	718	62	DSC[d]	Powder	He	11,12
	1100°C, 40min, Al_2O_3 crucible	B	684	739	55	DSC[d]	Bulk	He	11,12
	1100°C, 40min, Al_2O_3 crucible	B	676	739	63	DSC[d]	Powder	He	11,12
	1150°C, 40min, Pt crucible	B	619	718	99	DSC[c]	Bulk	Air	67
	1150°C, 2h, Pt crucible	C	669	724	55	DTA	Powder	Air	14
	1150°C, 30-40min, Al_2O_3 crucible	B	700	765	65	DTA[c]	-	-	24
$Bi_{2.7}SrCaCu_2O_y$	Containerless	C	652	718	66	DSC[d]	Bulk	He	11,12
	Containerless	C	630	700	70	DSC[d]	Powder	He	11,12
	1100°C, 40min, Al_2O_3 crucible	B	660	730	70	DSC[d]	Bulk	He	11,12
	1100°C, 40min, Al_2O_3 crucible	B	645	722	77	DSC[d]	Powder	He	11,12

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TABLE II (Continued)

$BiSrCaCu_3O_y$	1150°C, 2h, Pt crucible	C	673	707	34	DTA	Powder	Air	14
$Bi_2SrCaCu_3O_y$	1150°C, 2h, Pt crucible	C	667	705	38	DTA	Powder	Air	14
$Bi_3SrCaCu_3O_y$	1150°C, 2h, Pt crucible	C	645	688	43	DTA	Powder	Air	14
$Bi_3SrCaCu_3O_y$	1150°C, 2h, Pt crucible	C	643	703	60	DTA	Powder	Air	14
$Bi_4Sr_2Ca_2Cu_3O_y$	1150°C, 2h, Pt crucible	C	657	755	98	DTA	Powder	Air	14
$Bi_2Sr_2Ca_3Cu_4O_y$	1150°C, 2h, Pt crucible	C	703	743	40	DTA	Powder	Air	14
$Bi_2Sr_3Ca_3Cu_4O_y$	1150°C, 2h, Pt crucible	C	701	738	37	DTA	Powder	Air	14
$Bi_3Sr_3Ca_3Cu_4O_y$	1150°C, 2h, Pt crucible	C	700	777	77	DTA	Powder	Air	14
$Bi_4Sr_3Ca_3Cu_2O_y$	1150°C, 2h, Pt crucible	C	663	782	119	DTA	Powder	Air	14
$Bi_3Sr_3Ca_4Cu_5O_y$	1150°C, 2h, Pt crucible	C	704	738	34	DTA	Powder	Air	14
$Bi_4Sr_3Ca_3Cu_3O_y$	1050°C, 15min, Pt crucible	B	695	768	73	DSC	Bulk	-	63
$Bi_4Sr_3Ca_3Cu_4O_y$	1050°C, 15min, Pt crucible	B	690	750	60	DSC	Bulk	-	63
	1200°C, 15min, Pt crucible	B	689	745	56	DSC	Bulk	-	63
	1350°C, 15min, Pt crucible	B	675	707	32	DSC	Bulk	-	63
	1050°C, 15min, Pt crucible	B	673	748	75	DSC	Bulk	O_2	68
	1100°C, 30min, Pt crucible	B	683	731	48	DSC	-	-	20
	1200°C, 15min, Pt crucible	B	686	750	64	DSC	Bulk	O_2	68
	-	A	682	735	53	DSC	-	Air	64
	950°C, 2h, Al_2O_3 crucible	B	707	751	44	DTA	Bulk	-	19
	975-1075°C, Air, Ir crucible	C	683	733	50	DTA	-	O_2	8,9
	975-1075°C, Air, Ir crucible	C	683	723	40	DTA	-	N_2	8,9
	1150°C, 2h, Pt crucible	C	697	778	81	DTA	Powder	Air	14
$Bi_4Sr_3Ca_3Cu_5O_y$	1050°C, 15min, Pt crucible	B	686	743	57	DSC	Bulk	-	63

[a]A-Brass mold casting, B-Metal plate quench, C-Twin roller quench.

[b]Peak maximum temperature.

[c]5K/min.

[d]20K/min.

column of Table I, increased with the copper oxide content. Values of T_g and T_x decreased and the glass became thermally unstable, as indicated by a decrease in the value of $(T_x - T_g)$, with increase in glass melting temperature and also with total copper oxide content. This is due to a decrease in the number of glass network units, $[BiO_3]$ pyramids, with increase in $Cu(I)/Cu_{total}$ ratio and CuO content.

Values of T_g, T_x, and glass thermal stability expressed in terms of the parameter $(T_x - T_g)$ for Bi-Sr-Ca-Cu-O glasses of various compositions melted under different conditions are listed in Table II.

3.1.2. Bi-Pb-Sr-Ca-Cu-O System

A typical DSC scan [50] for the $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ glass showing T_g and the crystallization exothermic peak is presented in Fig. 8. The values of T_g, T_x, and the glass thermal stability parameter $(T_x - T_g)$ for Bi-Pb-Sr-Ca-Cu-O glasses of various compositions are listed in Table III. The values of T_g and T_x in the $Bi_xPb_{0.4}Sr_2Ca_2Cu_3O_y$ glasses slowly increase with the Bi_2O_3 content, reach a maximum for x ~ 3.0, and decrease with further increase in bismuth content as shown in Fig. 9 [72]. The
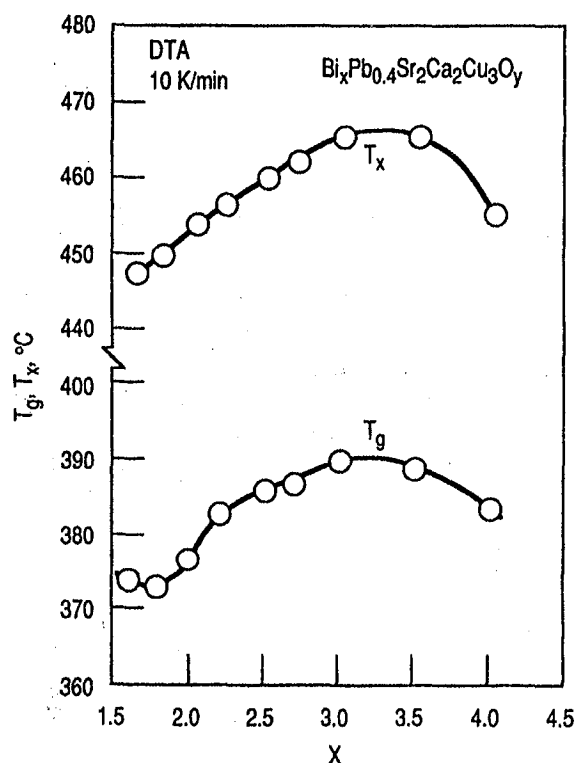

Fig. 9. Dependence of T_g and T_x of $Bi_xPb_{0.4}Sr_2Ca_2Cu_3O_y$ glasses on their bismuth content. [72]

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TABLE III. Compositions, Glass Transition Temperature (T_g), Crystallization Temperature (T_x), and Thermal Stability (T_x-T_g) of Bi-Sr-Ca-Cu-O Glasses Doped With Other Metal Oxides

Glass Composition	Glass Synthesis Method		T_g (K)	T_x(onset) (K)	T_x-T_g (K)	Technique (10K/min)	Sample Form	Atmosphere	Ref.
	Melting	Quenching[a]							
$Bi_{1.8}Pb_{0.2}Sr_2Ca_2Cu_3O_y$	Containerless	C	618	698	80	DTA	–	N_2 or air	13
$Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$	Containerless	C	613	683	70	DTA	–	N_2 or air	13
	1250°C, 20 min, Pt crucible	B	663	720[b]	57	DTA	–	Air	69
	1170°C, 10 min, Al_2O_3 crucible	B	661	719	58	DTA[c]	–	Air	66
	1250°C, 20 min, Al_2O_3 crucible	B	669	742[b]	73	DTA	–	–	52,53
	1150°C, 20 min, Al_2O_3 crucible	B	677	724	47	DSC[c]	Bulk	Air	70
$Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$	1025°C, 30 min, Pt crucible	B	656	714	58	DSC	Bulk	Ar	49,50
$Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_y$	Containerless	C	611	692	81	DTA	–	N_2 or air	13
$Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$	1250°C, 20 min, Pt crucible	B	670	718[b]	48	DTA	–	Air	69
$BiSrCaCu_2Al_{0.5}O_y$	1150°C, 30 min, Pt crucible	D	688	733(?)	45	DTA	Bulk	–	71
	1150°C, 30 min, Pt crucible	D	658	728(?)	70	DTA	Pressed powder	–	71
$Bi_4Sr_3Ca_3Cu_4O_y$ + 0.75 mole % V_2O_5	1200°C, ?	A	688	757	69	DSC	–	Air	64

[a] A-Brass mold casting, B-Metal plate quench, C-Twin roller quench, D-Pumping melt into silica tubes.

[b] Peak maximum temperature

[c] 5K/min

decreasing trend in values of T_g and T_x in $Bi_xPb_{0.4}Sr_2Ca_2Cu_3O_y$ glasses containing high Bi_2O_3 content is similar to that shown by Bi-based glasses [7,26]. The value of T_g and T_x for glasses in the $Bi_{2.9-z}Pb_zSr_2Ca_2Cu_3O_y$, $Bi_{3.4-z}Pb_zSr_2Ca_2Cu_3O_y$, and $Bi_{3.9-z}Pb_zSr_2Ca_2Cu_3O_y$ systems [72] decreased almost linearly with increase in Pb content implying that substitution of Pb for Bi does not improve the glass formation. This is expected because Bi_2O_3 acts as a glass former and a decrease in Bi_2O_3 content would degrade [73] the glass forming ability.

3.2. GLASS VISCOSITY

Glass fibers are generally pulled from a glass preform at a temperature around its softening point. A knowledge of the temperature dependence of the glass viscosity would be useful for successful drawing of continuous glass fibers.

Viscosities in the glass transition range for glasses of $Bi_xSrCaCu_2O_y$ (x = 1.5, 2.7) compositions, prepared [12] by metal-plate and twin-roller quenching methods, have been measured [12] using the beam-bending technique. Temperature dependence of viscosity in the 10^{10} to 10^{14} Pa.s range for the two glass compositions (Fig. 10 and 11), followed an Arrhenius behavior with an activation energy, E_η, of 800 to 980 kJ/mol. The glass having lower bismuth content showed larger E_η. Such a large value of E_η indicates that the Bi-Sr-Ca-Cu-O system forms a fragile liquid from which glass fibers may be drawn at around the glass softening point rather than from the melt because of high fluidity. The working range, $T_x - T_g$, for these glasses is also very narrow implying that crystallization would be a serious problem during fiber drawing at around the glass softening point. The glass working range needs to be extended in order to draw Bi-Sr-Ca-Cu-O fibers without devitrification. Although an increase in Bi content of the glass results in lower E_η, which is favorable for fiber drawing, this is unfortunately also accompanied [26] by a lowering of T_c of the glass ceramic. It is, therefore, necessary to find ways of lowering the activation energies of viscous flow and crystal growth without increasing the bismuth content in the glass.

The viscosity of a glass of $Bi_{1.5}SrCaCu_2O_y$ composition, prepared by melt quenching between metal plates, was determined [67] using a penetration method. Temperature dependence of viscosity in a very narrow temperature range is shown in Fig. 12. The shaded region shows the allowable fiber drawing range which is extremely narrow (704 to 707 K). The E_η is calculated to be 6300 kJ/mol which is very large compared to the value of 958 kJ/mol obtained using the beam bending method [12] for the same glass composition. This large difference in E_η values may be due to the different temperature ranges for viscosity measurements in the two studies and a non-Arrhenian temperature dependence of the glass viscosity.

Temperature dependence [64] of viscosity of $Bi_4Sr_3Ca_3Cu_4O_y$ glass is shown in Fig. 13. A beam-bending method and a rotational method were used for viscosity measurements in the range of $10^8 - 10^{15}$ poise and 0.1 - 100 poise, respectively. Temperature dependence of melt viscosity of the $Bi_2Sr_2Ca_1Cu_2O_y$ composition (Fig. 14) has been determined [74]. The melt viscosity varied from ~45 to 1 Poise in the temperature range 885 to 985 ^oC.
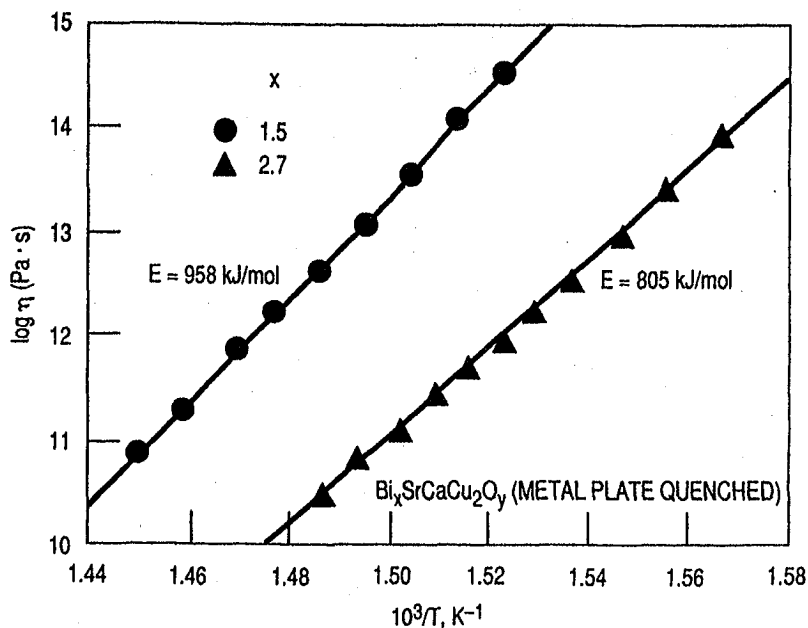
Fig. 10. Temperature dependence of viscosity of glasses of $Bi_xSrCaCu_2O_y$ compositions (x = 1.5, 2.7) prepared using metal-plate quenching technique. [12]
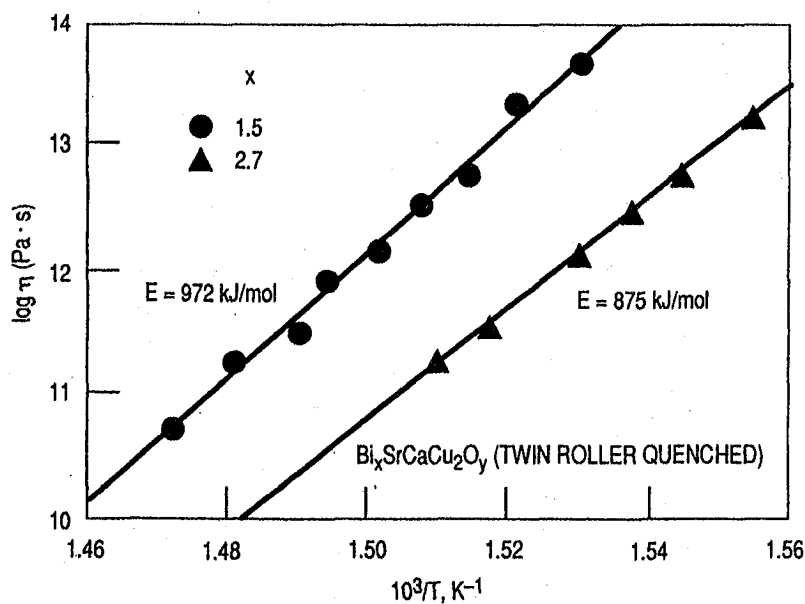

Fig. 11. Temperature dependence of viscosity of glasses of $Bi_xSrCaCu_2O_y$ compositions (x = 1.5, 2.7) prepared using metal twin-roller quenching technique. [12]
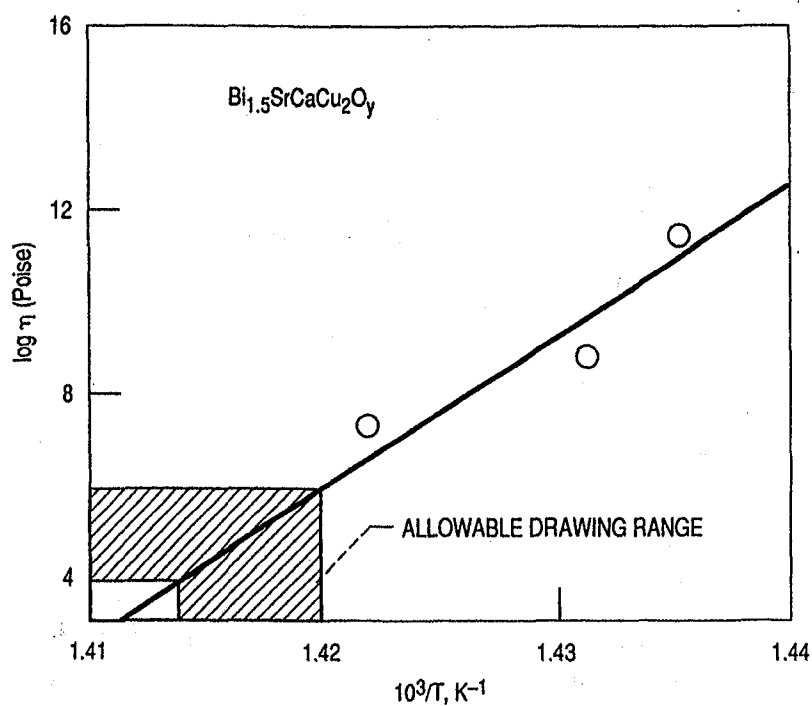
14

Fig. 12. Temperature dependence of viscosity of the melt quenched $Bi_{1.5}SrCaCu_2O_y$ glass. The allowable drawing range is shown as the shaded region. [67]
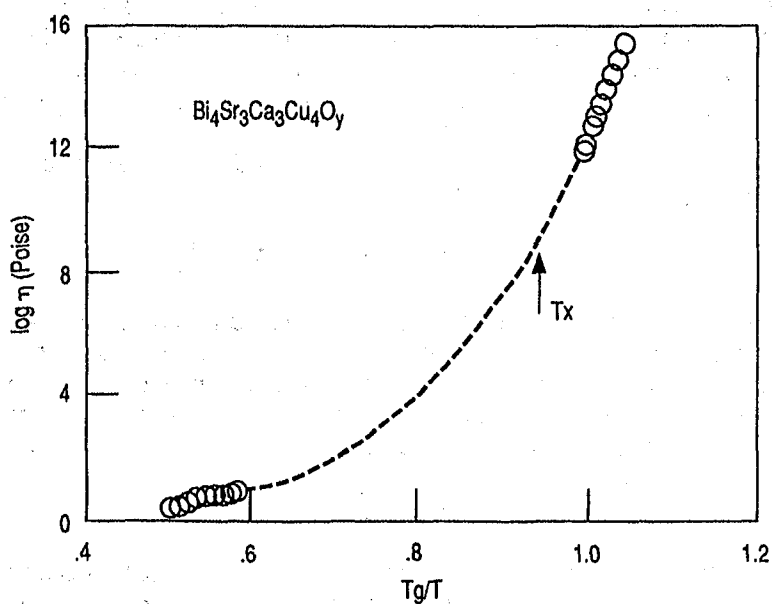

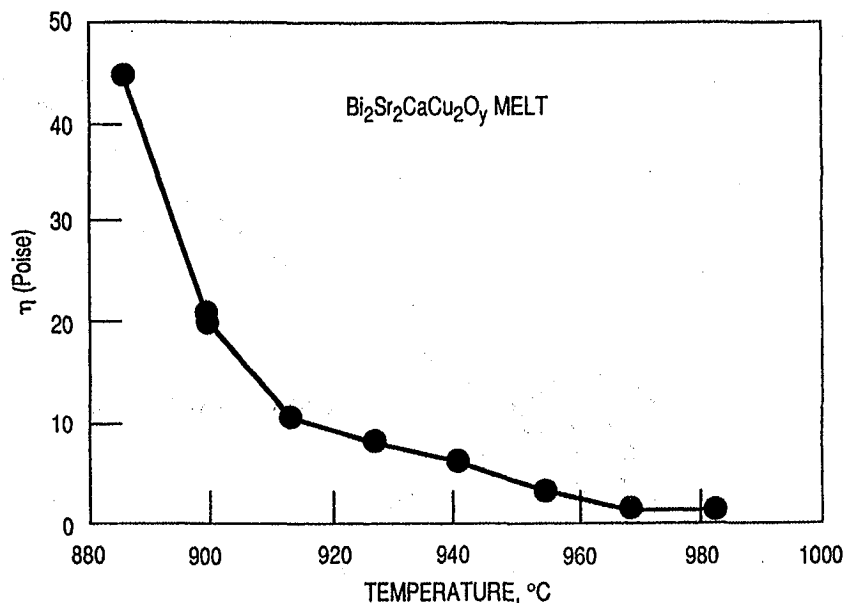Fig. 13. Temperature dependence of viscosity for the melt and glass of $Bi_4Sr_3Ca_3Cu_4O_y$ composition. [64]

15

Fig. 14. Temperature dependence of melt viscosity of
$Bi_2Sr_2CaCu_2O_y$ composition. [74]

3.3. CRYSTALLIZATION KINETICS

Devitrification of the Bi-Sr-Ca-Cu-O glasses is a serious
problem during fiber drawing by heating a glass preform to
around its softening point. Knowledge of the crystallization
kinetics of these glasses is, therefore, a prerequisite for
successful drawing of the glass fibers. Kinetics of
crystallization of the melt quenched Bi-Sr-Ca-Cu-O [11,17,68]
and (Bi,Pb)-Sr-Ca-Cu-O [50] glasses have been investigated by
isothermal [68] and non-isothermal [11,17,50] differential
scanning calorimetry (DSC).

The isothermal crystallization of a glass can be expressed
by the Avrami equation [75]:

$$x = 1 - \exp[-(kt)^n] \qquad (1)$$

where x is the volume fraction crystallized after time t, n the
Avrami parameter which depends on the crystal growth morphology,
and k the crystallization rate constant whose temperature
dependence (at least within narrow temperature ranges) can be
given by the Arrhenius equation:

$$k = \beta \exp[-E_a/RT] \qquad (2)$$

where β is the frequency factor, E_a the activation energy, R the
gas constant and T the isothermal absolute temperature. Taking
the logarithm of eq. (1) and rearranging gives

$$\ln[-\ln(1-x)] = n \ln k + n \ln t \qquad (3)$$

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TABLE IV. Crystallization Activation Energies of Bi-Sr-Ca-Cu-O
Glasses of Various Compositions by DSC

Glass Composition	Glass Melting and Quenching Method	E_a (kJ/Mol)	Technique	Atmosphere	Reference
$Bi_{1.5}SrCaCu_2O_y$	1100°C, 40 min, Al_2O_3 crucible Metal plate quenching.	412 (bulk) 389 (powder)	Non-isothermal	He	11
	Containerless melting twin roller quenching.	437 (bulk) 436 (powder)	Non-isothermal	He	11
	1300°C, 2 h, Pt crucible Metal plate quenching.	347\ bulk[a] 458/	Non-isothermal	Air	17,18
$Bi_{2.7}SrCaCu_2O_y$	1100°C, 40 min, Al_2O_3 crucible Metal plate quenching.	375 (bulk) 379 (powder)	Non-isothermal	He	11
	Containerless melting twin roller quenching.	391 (bulk) 419 (powder)	Non-isothermal	He	11
$Bi_4Sr_3Ca_3Cu_4O_y$	1050°C, 15 min., Pt crucible Metal plate quenching.	432 (bulk) 489 (bulk)	Non-isothermal Isothermal	O_2	68
	1200°C, 15 min., Pt crucible Metal plate quenching.	417 (bulk) 437 (bulk)	Non-isothermal Isothermal	O_2	68
$Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$	1025°C, 30 min., Pt crucible Metal plate quenching.	292 (bulk)	Non-isothermal	Ar	50

[a] Multiple crystallization peaks observed in DSC.

Isothermal DSC curves for crystallization of the glass are recorded at various temperatures. Values of n and k at a given temperature can be evaluated from an isothermal DSC scan via eq. (3) from the slope and intercept of a plot of $\ln[-\ln(1-x)]$ vs. $\ln t$. Values of E_a and ß can then be determined via eq.(2) from a plot of $\ln k$ vs. $1/T$.

In the nonisothermal method, DSC scans are recorded at various heating rates for the crystallization of a glass. Values of the kinetic parameters are calculated using the kinetic model of Bansal et al [76,77] which is expressed as:

$$\ln[T_p^2/\alpha] \;=\; \ln(E_a/R) - \ln ß + E_a/(RT_p) \qquad (4)$$

where T_p is the peak maximum temperature in the DSC, and α the heating rate. The position of the DSC crystallization peak shifts to higher temperature with increase in heating rate. Values of the crystallization kinetics parameters E_a and ß are determined via eq.(4) from a plot of $\ln[T_p^2/\alpha]$ vs. $1/T_p$.

The values of E_a for crystallization of glasses of various compositions are listed in Table IV and range from 292 to 489 kJ/mol. Values of E_a obtained by isothermal and nonisothermal DSC are in reasonably good agreement. Somewhat smaller values of E_a for the glasses made by metal-plate quenching than for the twin-roller quenched glasses may be due to a small difference in their compositions caused by the corrosion of an alumina crucible used in melting of the metal-plate quenched glasses. This could also result from the different Cu(I) contents of the two glasses as the amount of Cu(I) depends [13] on the cooling rate. The value of the Avrami exponent for crystallization of the $Bi_4Sr_3Ca_3Cu_4O_y$ glass was found [68] to be close to 3 suggesting a three dimensional crystal growth at a constant number of nucleation sites. Similar values of E_a for bulk and powder samples probably also suggest volume crystal growth in these glasses.

3.4. CRYSTAL PHASE(s) FORMATION ON HEAT TREATMENT OF GLASS

The development of crystalline phases on heat treatment of glasses of different compositions under various conditions of temperature, time, and atmosphere has been investigated by various researchers. Description of the results of all of these studies is beyond the scope of this chapter. Only typical results from a few selected studies are included here.

3.4.1. Bi-Sr-Ca-Cu-O System

Typical results [35] in the form of a temperature-time--transformation (T-T-T) diagram for the $BiSrCaCu_2O_y$ glass are given in Fig. 15. Each symbol denotes a mixture of crystalline phases as described in the figure caption. For example, the solid circle represents a mixture of the 80 K phase, CaO, and CuO. This figure consists of three different areas (I-III) containing various phases. Area I consists mainly of glassy phase along with a trace of CaO, area II mainly of the 80 K (2212) phase and CaO, and area III of the single 80 K phase. Area II is further divided into three sub-areas according to the nature of the minor phases present. Area II_1 also contains Cu_2O, area II_2 the CuO phase, and area II_3 neither CuO nor Cu_2O. The
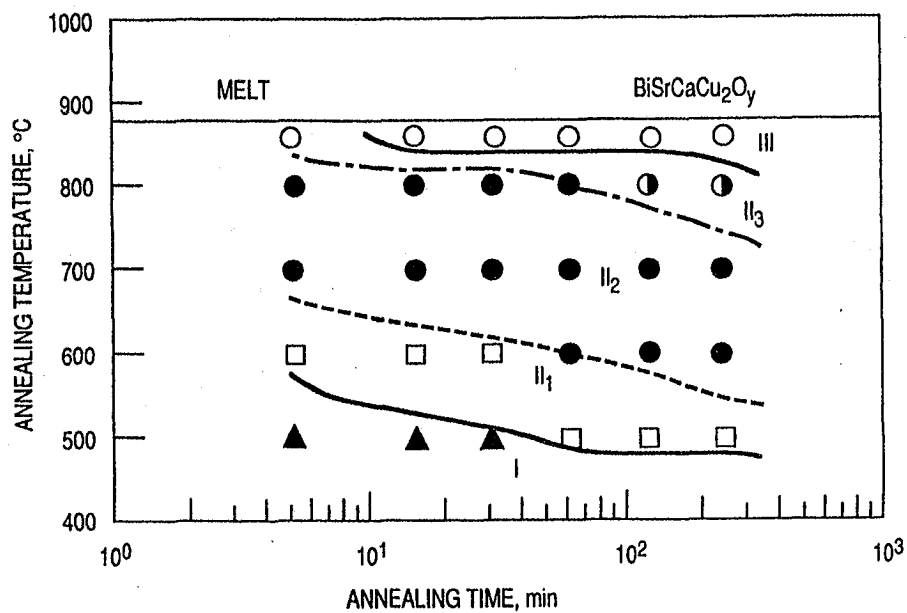
18

Fig. 15. T-T-T diagram for BiSrCaCu$_2$O$_y$ glass. ▲:glass (+CaO), □:
80 K phase + CaO + Cu$_2$O, ●: 80 K phase + CaO + CuO, ◐:
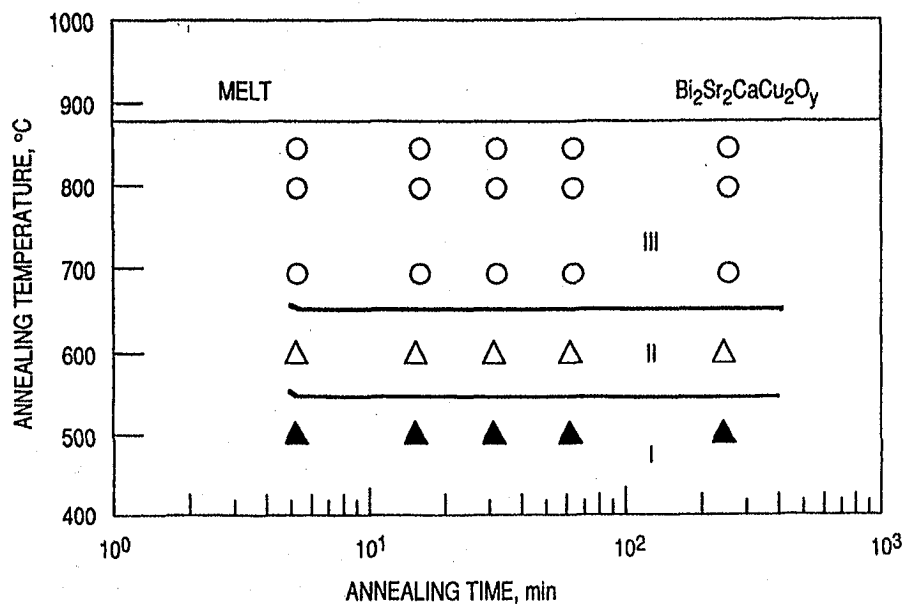80 K phase + CaO, O: 80 K phase. [35]

Fig. 16. T-T-T diagram for Bi$_2$Sr$_2$CaCu$_2$O$_y$ glass. ▲: glass, △: 10
K phase, O: 80 K phase. [35]

curves shown are drawn tentatively only as guides to the eyes. In this glass, CuO easily precipitates out and is present even after 800 °C annealing probably because of the high copper content in the glass. Also, the 10 K phase is not formed for any annealing conditions. Only the 80 K phase is formed on direct heat treatment at ~860 °C.

The T-T-T diagram [35] for $Bi_2Sr_2CaCu_2O_y$ glass (Fig. 16) is quite simple but different from those for the other two compositions. No crystalline phase is formed even after four hours of heat treatment at 500 °C. The 10 K (2201) phase crystallizes out when the glass is annealed at 600 °C and only the 80 K (2212) phase is formed when heat treated at or above 700 °C. The nature of the crystalline phases formed depends only on temperature, but is independent of the time of annealing.

Fig. 17 shows the T-T-T diagram [54] for the $Bi_2Sr_2Ca_2Cu_3O_y$ glass composition. Various symbols and the phases they denote are given in the figure caption. For example, closed triangles

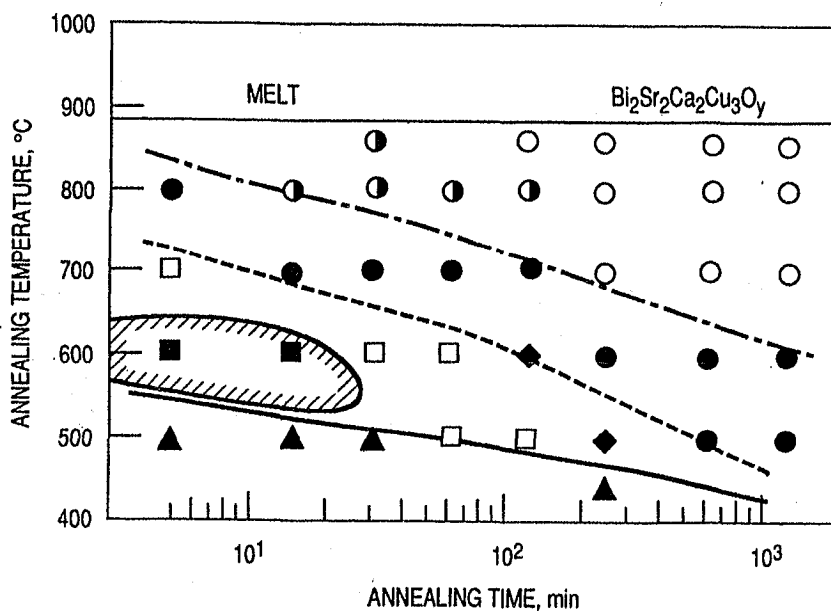Fig. 17. T-T-T diagram for $Bi_2Sr_2Ca_2Cu_3O_y$ glass. ▲: glass + Cu_2O + (CaO), ■: 80 K phase + CaO + 10 K phase + Cu_2O, □: 80 K phase + CaO + Cu_2O, ●: 80 K phase + CaO + CuO, ◆: 80 K phase + CaO + Cu_2O + CuO, ○: 80 K phase + CaO, O: 80 K phase. [54]
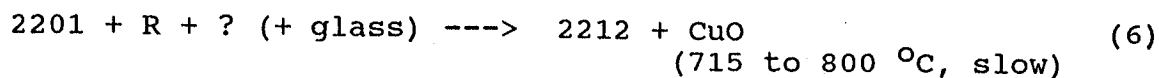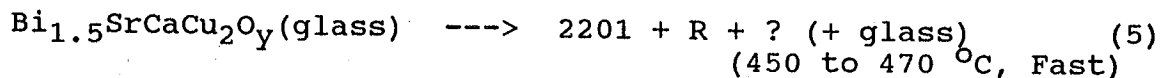
denote glassy phase with a trace of Cu_2O and residual CaO. For all the symbols other than the closed triangles, the 80 K (2212) HTS is the predominant crystalline phase. The solid line around 500 °C represents the boundary between glass and crystal regions and above this line the 2212 is the main crystalline phase in
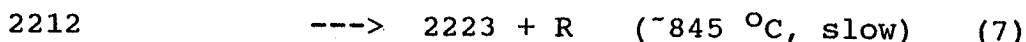
all cases. The 10 K phase is formed only on short heat treatments at around 600 °C as represented by the cross-hatched region. The boundary where the Cu(I) to Cu(II) transformation occurs is represented by the broken line and the dashed-and-dotted line indicates the boundary where CuO disappears. The temperature corresponding to each boundary decreases with increase in heat treatment time, implying that each solid state reaction depends on the heat treatment temperature and time. At temperatures over 700 °C and for heat treatment times longer than ~4 h, only the 110 K (2223) phase is formed in a wide region.

Transformation behavior [78] of the melt cast material of $Bi_2Sr_2CaCu_2O_x$ composition into the 2212 superconducting phase is different in air and nitrogen atmospheres. Due to a large fraction of copper ions present as Cu(I) in these materials, the crystallization mechanism is affected by the oxygen partial pressure. The DTA curves in air and nitrogen for the $Bi_2Sr_2Ca_2Cu_3O_y$ glass prepared by twin roller rapid quenching are different [13] from those made by the conventional metal plate quenching method. These results imply that the amount of Cu(I) ions in these glasses depends on the cooling rate and thus their crystallization behavior is affected by the conditions of glass synthesis. The glass preparation conditions have an effect [63] on the [Cu(I)]/[Cu_{total}] ratio in the glass which in turn affects the glass structure and its crystallization mechanism. The glasses melted at lower temperature have [63] lower values of [Cu(I)]/[Cu_{total}] and yield larger crystallites.

The initial crystalline phase precipitating out of the Bi-Sr-Ca-Cu-O glasses was 2201. The TGA scan for $Bi_4Sr_3Ca_3Cu_4O_y$ glass melted at 1050 °C showed [63] no weight gain in air in the temperature range corresponding to the first DTA exothermic peak which is ascribed to the crystallization of only the 2201 phase. Nassau *et al* [9] observed the formation of 2201 phase from Bi-glasses on heat treatment in nitrogen atmosphere implying that it is unnecessary to absorb oxygen from the atmosphere to form this phase. The mean valence of copper ions in this crystal phase is higher than in the parent glass indicating that crystallization is an oxidation process. Since no weight gain occurs during the first crystallization peak, the oxygen required for the crystal growth must come from the glassy matrix. It is, therefore, anticipated that glasses with low $Cu(I)/Cu_{total}$ ratio produce larger 2201 crystals and vice versa. It should, therefore, be possible to retard the crystallization by controlling the atmosphere and the $Cu(I)/Cu_{total}$ ratio since the crystal growth needs oxygen and the crystal size depends on the $Cu(I)/Cu_{total}$ ratio. Continuous glass fibers have been successfully drawn [64] at a temperature above T_x from a Bi-Sr-Ca-Cu-O glass preform having a high value of $Cu(I)/Cu_{total}$.

On reheating glass of $Bi_{1.5}SrCaCu_2O_y$ composition in air, the following crystallization events are proposed [17] to occur:

$$Bi_{1.5}SrCaCu_2O_y (glass) \longrightarrow 2201 + R + ? (+ glass) \quad (5)$$
$$(450 \text{ to } 470 \text{ °C, Fast})$$

$$2201 + R + ? (+ glass) \longrightarrow 2212 + CuO \quad (6)$$
$$(715 \text{ to } 800 \text{ °C, slow})$$

$$2212 \quad\quad\quad \longrightarrow \quad 2223 + R \quad\quad (\tilde{}845\ ^oC,\ slow) \quad\quad (7)$$

where R is $Bi_{2+x}Sr_{2-x}CuO_y$ and ? represents an unidentified phase.

Several mechanisms have been proposed [79] for formation of the 2223 phase but the exact mechanism is not known at the present time. One possibility is the disproportionation [80] of 2212 at just below the melting point into 2223 and 2201:

$$2Bi_2Sr_2CaCu_2O_8 \quad\quad \longrightarrow \quad\quad Bi_2Sr_2Ca_2Cu_3O_{10} + Bi_2Sr_2CuO_6 \quad (8)$$
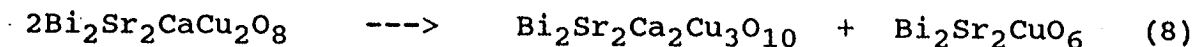
In the opinion of the present reviewer, the possibility of the disproportionation mechanism is unlikely. If excess CuO and CaO or some compounds containing both copper and calcium oxides such as Ca_2CuO_3 are present adjacent to the 2212 phase, the following reaction may occur

$$Bi_2Sr_2CaCu_2O_8 + CuO + CaO \quad \longrightarrow \quad Bi_2Sr_2Ca_2Cu_3O_{10} \quad\quad (9)$$
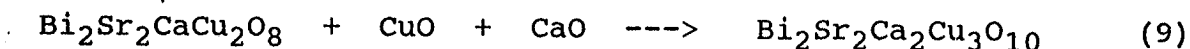
provided that the 2223 phase is thermodynamically stable under the experimental conditions. The 2223 phase can also be produced by the following reaction:

$$Bi_2Sr_2CuO_6 + 2CuO + 2CaO \quad \longrightarrow \quad Bi_2Sr_2Ca_2Cu_3O_{10} \quad\quad (10)$$
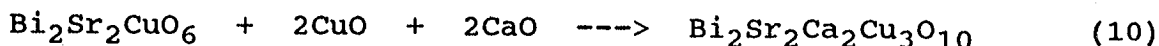
The 2223 phase may also form [81] by precipitation from a partially melted liquid. Development of the 2223 phase on heat treatment of a melt-quenched $Bi_2Sr_2Ca_4Cu_5O_y$ material at 865 ^oC has been followed [21] by electron microscopy, XRD, and EDS. The high T_c phase developed from the 80 K phase which in turn formed from the 2201 phase. Lattice imaging was employed to follow the conversion of 2212 phase into 2223. Presence of a liquid phase rich in Cu and Ca near the solid-liquid interface was essential for the evolution of the 110 K phase at 865 ^oC. According to Luo *et al* [82], 2223 is formed through a peritectic or peritectic-like melting of 4334 phase at $\tilde{}863\ ^oC$ in air:

$$4334(solid) \quad \longrightarrow \quad liquid + 2223(solid) + O_2 \quad (\tilde{}865-870 ^oC) \quad (11)$$
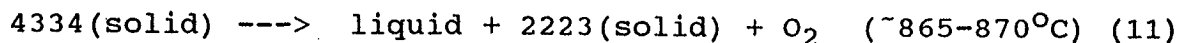
The 2223 has a plate-like morphology and is bounded by an amorphous phase. A thin layer of 4334 is also systematically observed between 2223 and the amorphous phase. The conditions for preparation of the 2223 phase are very critical because of the long range diffusion involved, the locally nonequilibrated oxygen partial pressure, and especially the narrow temperature stability domain of 2223. Starting from the peritectic decomposition of 4334, it would be very difficult to prepare 2223 with good properties due to the coexistence of a 4334, 2234, and 2223 intergrowth composite microstructure on a very fine scale. This microstructure may result in low J_c and a broad superconducting transition.

A single superconducting 110 K phase material has been prepared [30,32] by crystallization of $Bi_2Sr_2Ca_3Cu_4O_y$ and $Bi_2Sr_2Ca_4Cu_5O_y$ glasses at 870 ^oC for 10 days in air. The starting composition as well as the annealing parameters are important in forming the 110 K phase. The 80 K and Ca_2CuO_3

TABLE V. Transition Temperatures and the Phases Formed in
$Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ Glass Samples Annealed in
Air Under Different Conditions [50]

Sample	Heat Treatment			$T_c(R=0)$ (K)	Phases Identified From Powder XRD
	Temp. (°C)	Time (h)	Cooling Rate		
BI-0	–	–	–	–	Amorphous, CaO(trace)
BI-1	500	24	Slow	–	2201[a]
BI-2	720	24	Slow	75	2212[b], 2201, Ca_2PbO_4, CuO
BI-3	750	24	Slow	<63	2212, 2201, Ca_2PbO_4, CuO
BI-4	802	25	Slow	69	2212, 2201, Ca_2PbO_4, CuO
BI-5	840	24	Slow	68	2212, 2223[c], 2201, Ca_2PbO_4
BI-6	840	94	Slow	98	2223, 2212, 2201, Ca_2PbO_4
BI-7	840	94	Fast	68	2223, 2212, Ca_2PbO_4
BI-9	840	243	Slow	107.2	2223, 2212, Ca_2PbO_4
BI-8	850	94	Slow	<77	2212, 2223, Ca_2PbO_4

[a] $Bi_2Sr_2Ca_0Cu_1O_6$
[b] $Bi_2Sr_2Ca_1Cu_2O_8$
[c] High-T_c phase isomorphic with $Bi_2Sr_2Ca_2Cu_3O_{10}$

phases first coprecipitate from the glass. The 110 K phase
nucleates and grows at the interface between these two phases
which is controlled by interface diffusion of calcium and
copper.

3.4.2. Bi-Pb-Sr-Ca-Cu-O System

Formation of crystalline phases on thermal treatment of
Pb-doped glasses of different compositions has been investigated
by a number of researchers. The development [50] of various
crystalline phases on heat treatment of a glass of
$Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ composition under different conditions is
given in Table V. Typical results in the form of T-T-T diagrams
are [54] presented in Fig. 18 for $Bi_{1.8}Pb_{0.2}Sr_2Ca_2Cu_3O_y$ and in
Fig. 19 for $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ glass compositions. In the
figures, each symbol represents the crystalline phases formed on
heat treatment of the glass at a given temperature and time. For
example, the closed triangles represent the glassy phase along
with a trace of Cu_2O and residual CaO. The double squares
represent a mixture of the 2212 phase, a trace of CaO, and
Ca_2PbO_4. Various other symbols and the phases they denote are
listed in the figure captions. The solid, broken, and
dashed-and-dotted boundary lines are the same as in Fig. 17 for
$Bi_2Sr_2Ca_2Cu_3O_y$. The 110 K phase appears above the bold boundary
line around 850 °C. The cross-hatched area represents the
presence of the 10 K phase. Ca_2PbO_4 is observed in the area
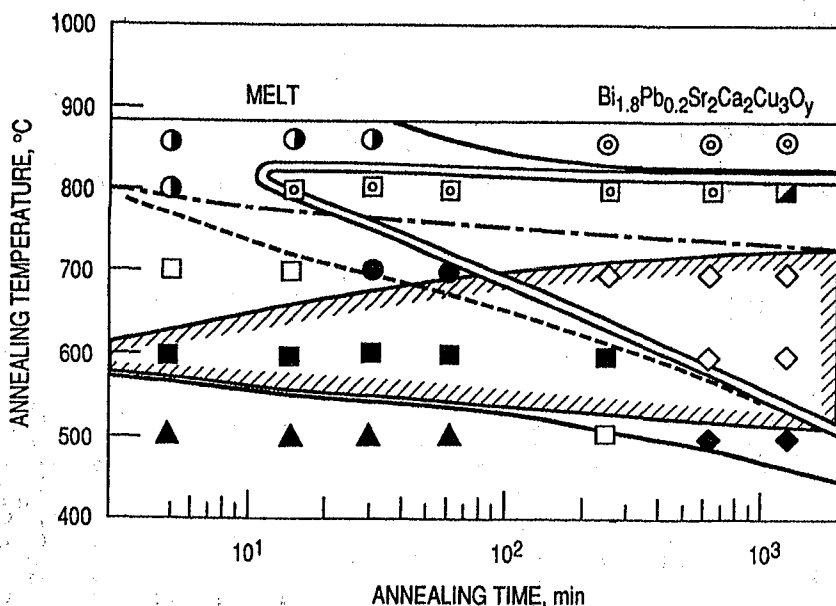within the double boundary lines.

Fig. 18. T-T-T diagram for $Bi_{1.8}Pb_{0.2}Sr_2Ca_2Cu_3O_y$ glass. ▲: glass
+ Cu_2O + (CaO), ■: 80 K phase + CaO + 10 K phase   + Cu_2O, □:
80 K phase + CaO + Cu_2O, ●: 80 K phase + CaO + CuO, ♦: 80 K
phase + CaO + Cu_2O + CuO, ◇: 80 K phase + CaO + CuO + 10 K
phase + Ca_2PbO_4, ◐: 80 K phase + CaO, ▣: 80 K phase + CaO +
Ca_2PbO_4, ▨: 80 K phase + Ca_2PbO_4, ◉: 80 K phase + CaO + 110
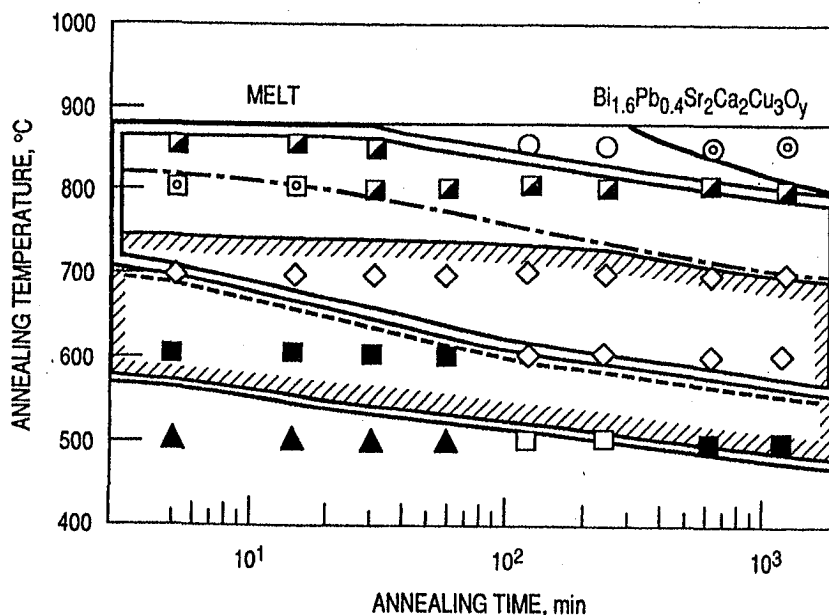K phase, ◎: 80 K phase + 110 K phase. [54]

1000

900 — MELT $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$

ANNEALING TEMPERATURE, °C

800

700

.600

500

400

          10^1 10^2 10^3

ANNEALING TIME, min

Fig. 19. T-T-T diagram for $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ glass. ▲: glass + Cu_2O + (CaO), ■: 80 K phase + CaO + 10 K phase + Cu_2O, □: 80 K phase + Cu_2O, ◇: 80 K phase + CaO + CuO + 10 K phase + Ca_2PbO_4, ▣: 80 K phase + CaO + CuO + Ca_2PbO_4, ◪: 80 K phase + Ca_2PbO_4, O: 80 K phase, ◉: 80 K phase + 110 K phase. [54]

In Figs. 17, 18, and 19 the formation, transformation, and disappearance of copper oxides are quite similar, yet the regions of the 10 K phase formation are different. The regions of 10 K phase formation (the cross-hatched area) and Ca_2PbO_4 formation (surrounded by double lines) tend to extend with an increase in Pb content. The major difference between Fig. 18 and 19 is that both the 10 K phase and Ca_2PbO_4 are easily formed even at short annealing times in the Pb-rich glass. However, at long annealing times the formation patterns of both phases are similar. The large region for formation of Ca_2PbO_4 in the lead rich glass may be explained [54] by the fact that this compound consists of only Pb and Ca oxides. The production of this Ca-rich Ca_2PbO_4 would enhance the formation of a Ca-deficient phase such as $Bi_2Sr_2CuO_6$.

Ca_2PbO_4 is formed [54] in $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ glass (Fig. 19) on short term annealing at 855 °C. However, after long term annealing Ca_2PbO_4 disappears and the 110 K phase is formed implying that Ca_2PbO_4 plays an important role in the production of the high-T_c phase. Probably the Ca_2PbO_4 melt formed at ~850 °C reacts with 2212 and CuO to produce 2223.

The following crystallization sequence on heat treatment of the $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ glass in air has been proposed [15, 50]. The 2201 phase first precipitates out followed by formation

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of the 2212 phase at higher temperature. The 110 K T_c phase is formed at still higher temperature just below the melting point probably by reaction between the low-T_c 2201 and 2212 phases and the residual calcium and copper oxides. The high-T_c phase formation rate is sluggish and takes a long time (days) due to the relatively long-range diffusive ordering involved. Even after prolonged heating of the glass at 840 $^\circ$C for more than ten days, the product contained an appreciable amount of the 80 K phase in addition to the 110 K phase. TGA curves [15,50] in oxygen (Fig. 20) showed that formation of the 2212 phase is accompanied by a rapid absorption of O_2 and no uptake of O_2 occurs during the formation of the 2201 phase at low temperature or when the high-T_c 2223 phase is produced at 840 $^\circ$C.
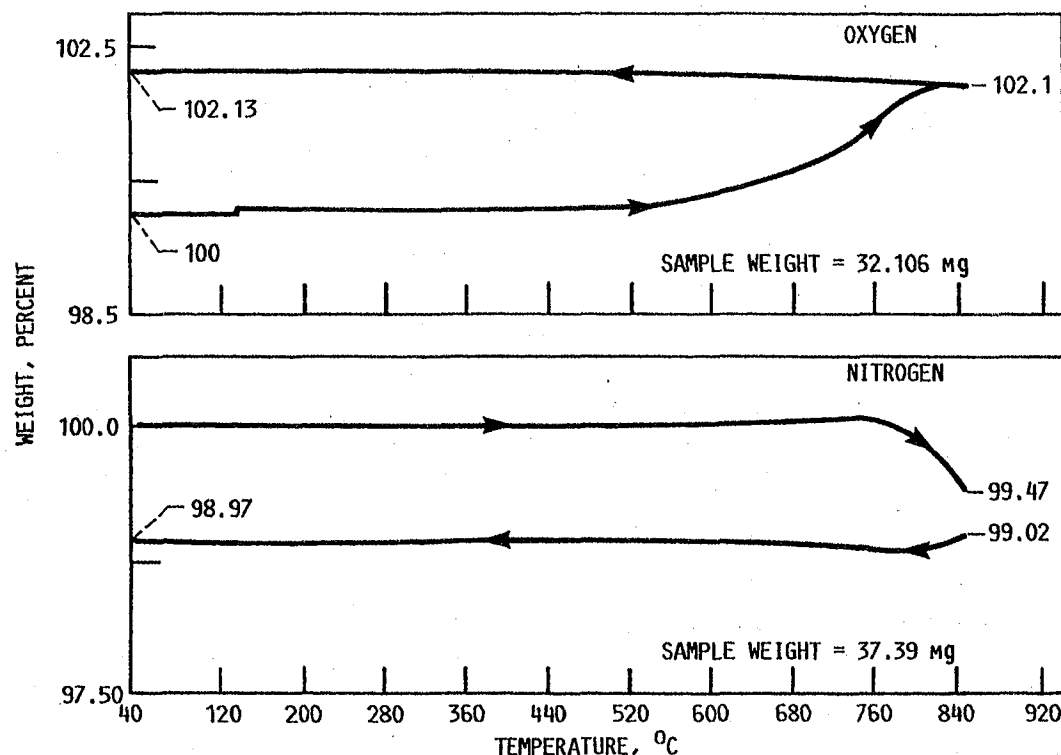

Fig. 20. TGA scans of $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ glass at heating and cooling rates of 5°C/min in oxygen and nitrogen. [50].

Glass of $Bi_{1.84}Pb_{0.34}Sr_2Ca_2Cu_4O_y$ composition annealed at 842 $^\circ$C for >48 h in Ar+O_2 atmosphere, mainly contains [83] the 110 K phase. The formation of the 110 K phase appears not to be the result of disproportionation. It is suggested [83] that a liquid phase is formed which causes dissolution of the low-T_c phase in the melt and precipitation of the 110 K phase.

3.5. EFFECTS OF PROCESSING CONDITIONS ON T_c AND J_c
The superconducting properties of the glass-ceramics are sensitive to the composition and are also dependent on the glass melting temperature and quenching rate, annealing temperature, time, atmosphere, and cooling conditions. Description of the results for all of the glass compositions which have been

studied is beyond the scope of this chapter. Only typical results from a few selected studies are included here.

3.5.1. Bi-Sr-Ca-Cu-O System

The effect of bismuth content on $T_c(R=0)$ of the samples annealed for 40 h in air at 820 $^\circ$C in the $Bi_xSrCaCu_2O_y$ system is shown [26] in Fig. 21. The T_c tend to decrease with increase in Bi_2O_3 content. The influence of calcium content on $T_c(R=0)$ of the samples obtained by annealing at 820 $^\circ$C for 40 h in air in the $Bi_{1.2}SrCa_zCu_2O_y$ system is given [26] in Fig. 22. The T_c value is ~75 K irrespective of the CaO content.
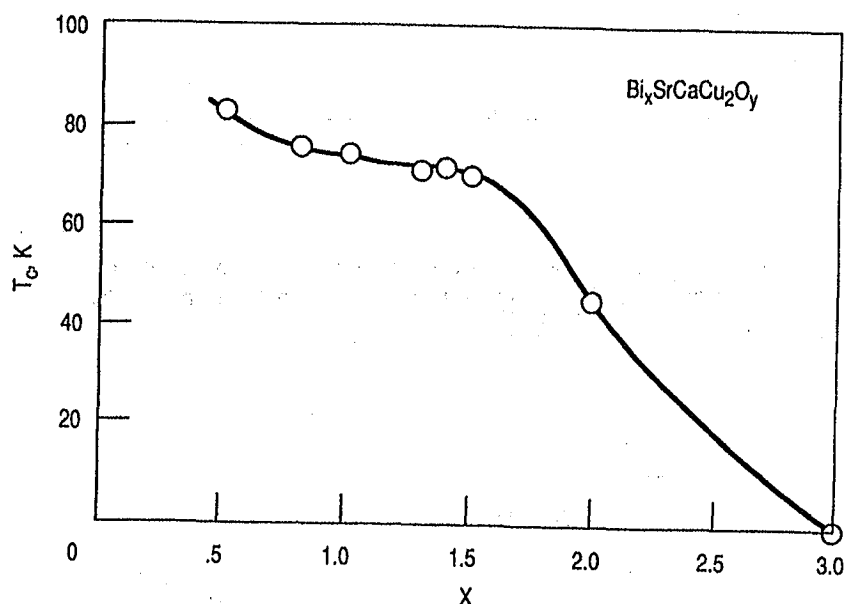

Fig. 21. Superconducting transition temperatures, $T_c(R=0)$, of $Bi_xSrCaCu_2O_y$ glasses annealed at 820 $^\circ$C for 40 h in air and furnace cooled. [26]

Effect of annealing temperature on T_c of glass-ceramics of different compositions has been studied by various workers. Typical resistivity vs. temperature curves for glass samples of $Bi_{1.2}SrCaCu_2O_x$ compositions [27] annealed for 20 h at various temperatures in air and furnace cooled and their T_c are shown in Fig. 23. The T_c increased with increase in annealing temperature. The influence of annealing temperature on T_c and J_c of $Bi_2Sr_2CaCu_2O_y$ glass-ceramics are presented [27] in Fig. 24. The glass samples were annealed in air for 48 h and fast quenched. The T_c increased with increase in the annealing temperature, reached a maximum and than fell when the annealing temperature was further raised.

The influence of annealing time on T_c and J_c (at 77 K and zero magnetic field) of $Bi_2Sr_2CaCu_2O_y$ glass samples annealed at 820 $^\circ$C in air and furnace cooled is shown [28] in Fig. 25.

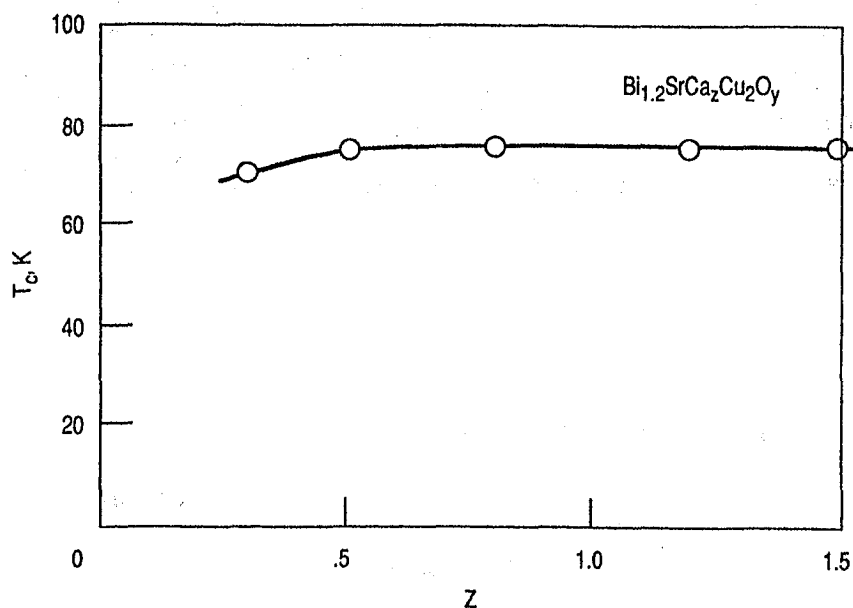Fig. 22. Superconducting transition temperatures, $T_c(R=0)$, of $Bi_{1.2}SrCa_zCu_2O_y$ glasses annealed at 820 $^\circ C$ for 40 h in air and furnace cooled. [26]
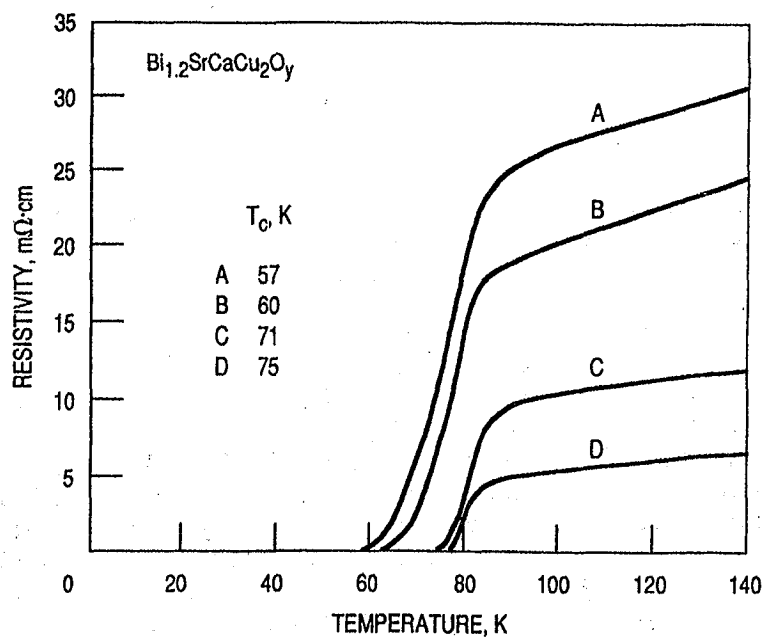

Fig. 23. Temperature dependence of electrical resistivity of $Bi_{1.2}SrCaCu_2O_y$ glass samples annealed for 20 h in air at various temperatures and furnace cooled. A: 760 $^\circ C$, B: 800 $^\circ C$, C: 840 $^\circ C$, and D: 850 $^\circ C$. [27]
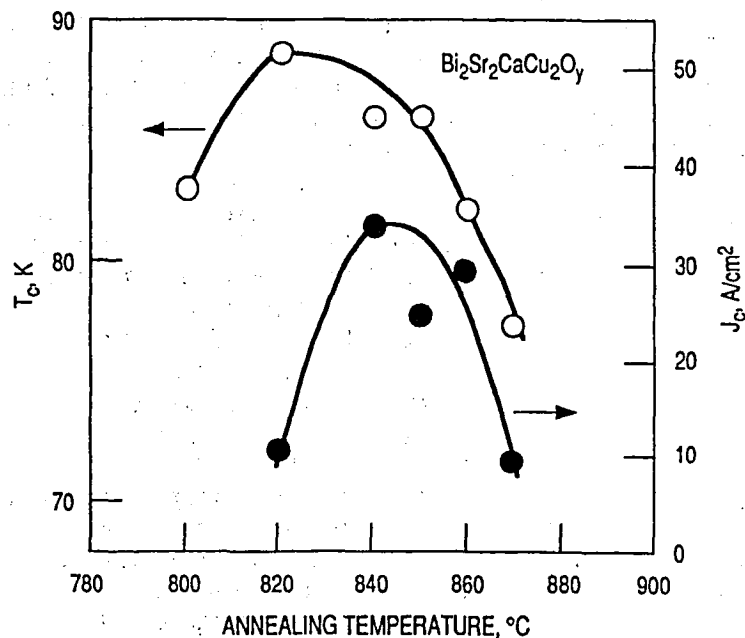
Fig. 24. Effect of annealing temperature on critical temperature T_c and critical current density J_c (77 K, zero magnetic field) of $Bi_2Sr_2CaCu_2O_y$ glass samples annealed in air for 48 h and air-quenched. [27]

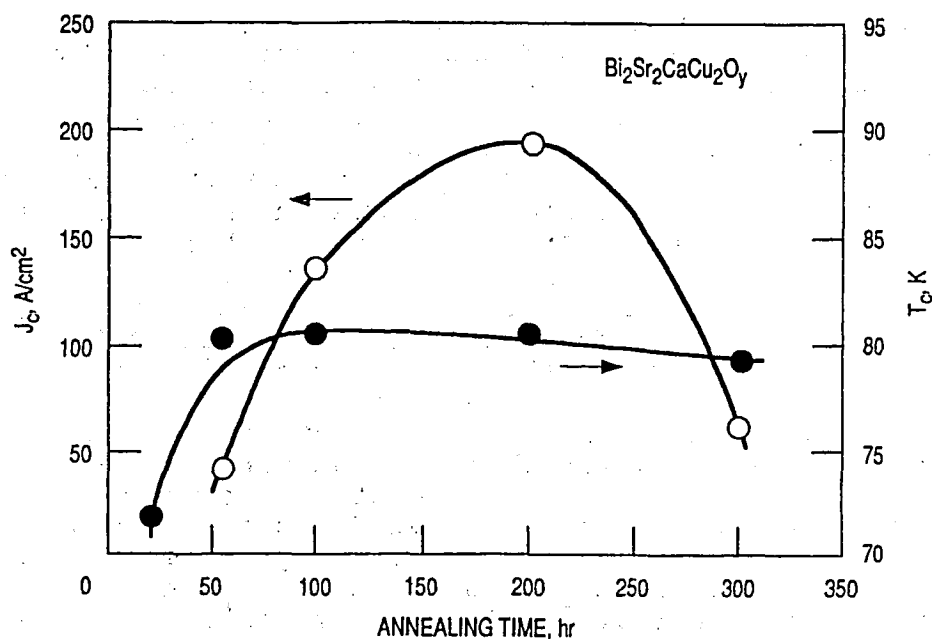Fig. 25. Values of critical temperature T_c and critical current density J_c (77 K, zero magnetic field) of $Bi_2Sr_2CaCu_2O_y$ glass samples annealed at 820 °C in air for various times and furnace cooled. [28]

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Specimens annealed for 50 - 200 h had T_c of 80 K. The sample annealed for 200 h showed the highest J_c of 200 A/cm^2. The 840 ^oC annealed specimens also exhibited similar [28] behavior. Weak links at the grain boundaries are responsible for low values of J_c in these glass ceramics. The density of weak links at the grain boundaries needs to be reduced in order to improve the J_c.

The effect of annealing atmosphere (O_2, air, or vacuum) on T_c of glasses of $BiSrCaCu_2O_y$, $Bi_2Sr_2Ca_2Cu_3O_y$, $Bi_3Sr_3Ca_3Cu_4O_y$, and $Bi_3Sr_3Ca_4Cu_5O_y$ compositions annealed for 24 or 48 h at 870 to 880 ^oC has been investigated [14]. Annealing in O_2 greatly enhanced the 110 K transition. The samples annealed in air showed transitions at 110 and 85 K whereas only the 85 K transition along with a long tail extending below 77 K was observed in the vacuum-annealed specimens.

The rate at which the sample is cooled after annealing also affects its superconducting behavior. A glass of $Bi_{1.5}SrCaCu_2O_y$ composition heat treated at 845 ^oC for 88 h in air followed by fast cooling showed [17,18] semiconducting behavior in the normal state, a 50% drop in resistance at 88 K, and a broad resistive tail with $T_c(R=0)$ of 11 K. In contrast, another sample similarly annealed, but slow cooled, was metallic in the normal state, exhibited a small resistivity drop at 108 K, a major drop at 87 K, and $T_c(R=0)$ of 55 K. The sample annealed for 168 h at 845 ^oC in air and furnace cooled exhibited a $T_c(R=0)$ at 77 K. However, a $BiSrCaCu_2O_y$ glass sample annealed at 850 ^oC for 24 h in oxygen and cooled rapidly showed [23] a sharp superconducting transition and higher T_c whereas the furnace cooled sample exhibited a broad transition with a tail and low T_c. The effect of cooling conditions on the superconducting properties of $Bi_{1.2}SrCaCu_2O_y$ and $Bi_2Sr_2CaCu_2O_y$ glass-ceramics has also been investigated [27]. Two glass specimens of $Bi_{1.2}SrCaCu_2O_y$ compositions were annealed at 880 ^oC for 20 h in air and one was rapidly quenched in air and the other was furnace cooled. The temperature dependence of electrical resistivity of these samples is shown in Fig. 26. The quenched sample has a high normal state resistivity with a sharp drop at ~90 K followed by a long tail which persists to very low temperatures. On the other hand, the furnace cooled sample shows a much smaller value of normal state resistivity. Also, it exhibits a drop in resistivity at ~105 K indicating the formation of the high-T_c phase followed by a sharp drop at ~85 K with a $T_c(R=0)$ of ~68 K. The effect of cooling conditions on the value of T_c of the glass ceramics obtained by annealing a glass of $Bi_2Sr_2CaCu_2O_y$ composition at 820 ^oC for 48 h in air differs from that for the $Bi_{1.2}SrCaCu_2O_y$. The normal state resistivity of the furnace cooled sample was smaller than for the air quenched sample, but the former showed a $T_c(R=0)$ value of 85 K compared with 88 K for the latter. The reason for this difference in behavior is not clear. The influence of various cooling rates on T_c of $BiSrCaCu_2O_y$, $Bi_2Sr_2Ca_2Cu_3O_y$, $Bi_3Sr_3Ca_3Cu_4O_y$, and $Bi_3Sr_3Ca_4Cu_5O_y$ glasses annealed for 24 or 48 h at 870 to 880 ^oC in air, O_2, or vacuum has also been studied [14]. The T_c(onset) increased with decrease in cooling rate.

The Bi-Sr-Ca-Cu-O glasses are deficient in oxygen as indicated by appreciable weight gains [7,9,14,17,18] starting at ~500 ^oC in the TGA scans in oxygen-containing atmospheres and also from the results of Table I. The weight increase is caused
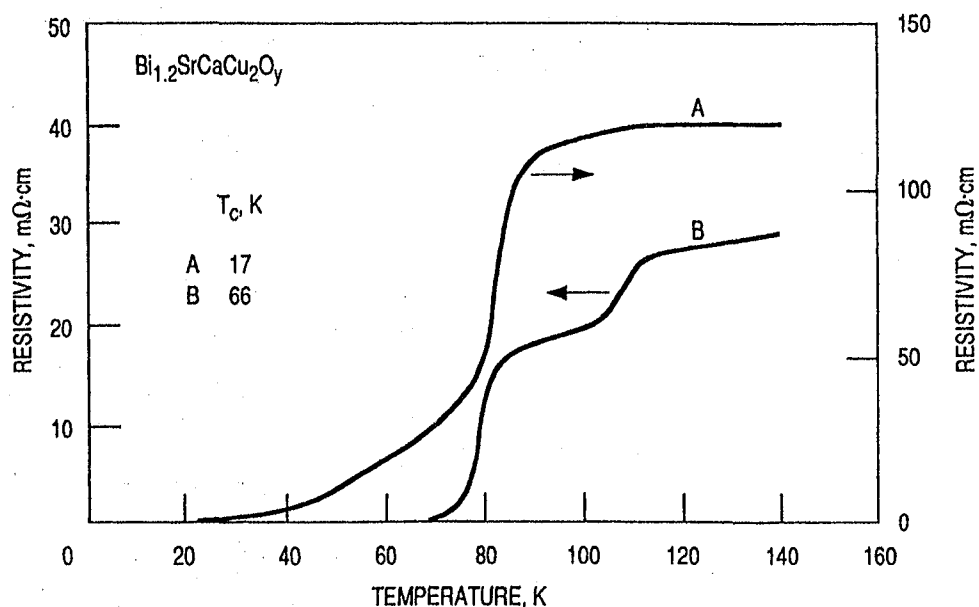
30

Fig. 26. Effect of cooling rate on the temperature dependence of electrical resistivity of $Bi_{1.2}SrCaCu_2O_y$ glass samples annealed in air at 880 °C for 20 h and (A) air-quenched, and (B) furnace cooled. [27]
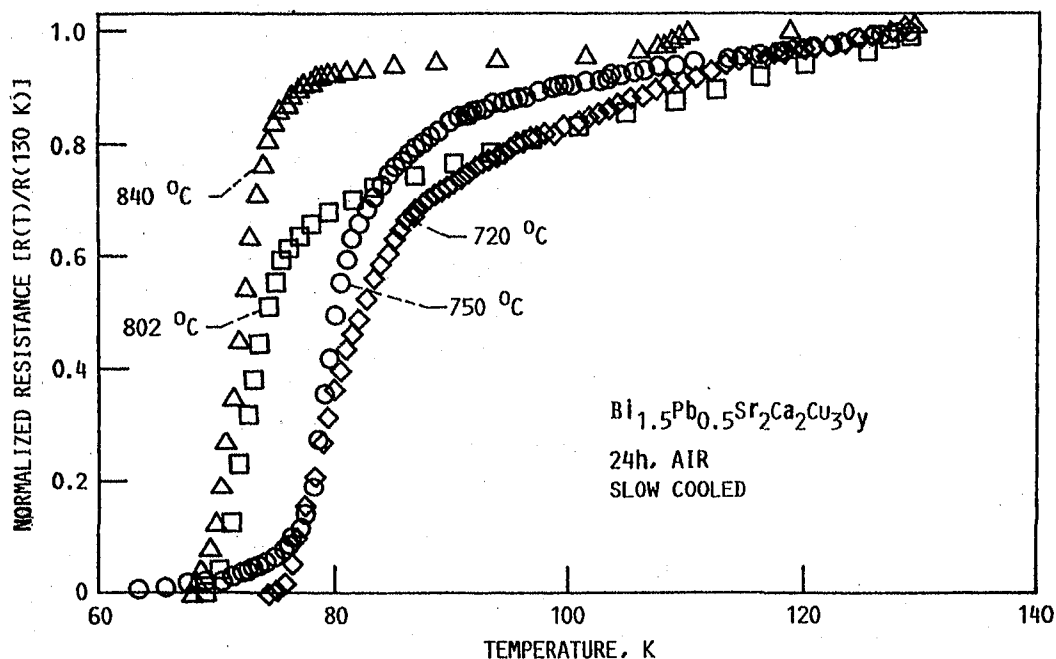

Fig. 27. Temperature dependence of electrical resistance of $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ glass specimens annealed for 24 h in air at various temperatures and furnace cooled. [50]

by the oxidation of Cu(I) to Cu(II). The amount of oxygen absorption increased with the CuO content in the glasses which may be due to an increase in their Cu(I) concentration. Also, these glasses lose O_2 at high temperatures as indicated by weight loss in the TGA scans [7,9,14]. An increase in the cooling rate and/or the annealing temperature would result in higher deficiency of oxygen in these glass-ceramics. Therefore, a lower T_c of the materials annealed in oxygen-deficient atmosphere or those fast cooled after annealing may be ascribed to the deficiency of oxygen.

3.5.2. Bi-Pb-Sr-Ca-Cu-O System

The annealing temperature greatly effects the nature of the phase formation in the glass-ceramic samples and their T_c. Temperature dependence of electrical resistance of the $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ glass specimens annealed at different temperatures for 24 h in air and furnace cooled is shown in Fig. 27 and the results are summarized in Table V. The as-quenched glass was an insulator and the sample annealed at 500 °C was semiconducting. The specimen heat treated at 720 °C showed $T_c(R=0)$ of 75 K. The sample annealed at 750 °C showed a sharp drop in resistance, but had a long tail and the resistance did not become zero even at 63 K. The 802 °C annealed sample had a sharp resistivity drop starting at ~80 K with $T_c(R=0)$ of 69 K. The specimen heat treated at 840 °C for 24 h showed a small drop in resistance at ~110 K, and a sharp transition at ~78 K with $T_c(R=0)$ at 68 K. Annealing at 850 °C resulted in partial melting and a long tail in the resistance vs. temperature curve with $T_c(R=0) < 77K$. An annealing temperature of 840 °C appears to be optimum for formation of the 110 K phase for this glass composition. In $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ glass, the highest $T_c(R=0)$ of 106 K was observed [58] in the sample annealed at 845 °C for 24 h in air. The T_c decreased when the annealing temperature was raised further.

The influence of annealing time at 840 °C in air on 110 K phase formation in $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ glass is shown [50] in Fig. 28 and Table V. The zero resistance temperature increased with the time of annealing at 840 °C. The specimen annealed for 243 h and furnace cooled exhibited a very sharp transition with $T_c(R=0)$ of 107.2 K. The $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ glass samples annealed at 845 °C in air showed [58] a fixed value of $T_c(R=0)$ of 106 K for annealing times longer than 24 h. However, the J_c value increased with the annealing time probably due to an increase in the volume fraction of the 110 K phase. These results indicate slow kinetics of the 110 K phase formation reaction resulting in the need for very long annealing times for formation of glass-ceramic samples having an appreciable amount of the high-T_c phase and showing high T_c and J_c.

The effects of annealing in air or nitrogen atmospheres on the formation of HTS phases in $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ have been studied [84]. The fraction of the high-T_c phase increased with sintering time in air, and there was virtually no effect even after annealing for 264 h in N_2. The absence of oxygen favored the formation of the low-T_c phase and inhibited the formation of the high-T_c phase. These results are further substantiated from the TGA scans [15,50] shown in Fig. 20. At high temperature, a gain in sample weight is observbed in O_2 while
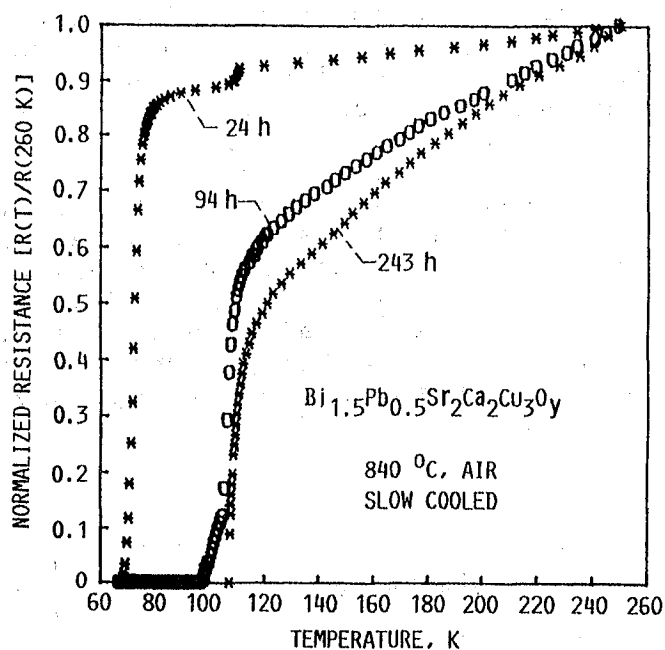
Fig. 28. Influence of annealing time on temperature dependence
of electrical resistance of the $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$
glass annealed in air at 840 °C and furnace cooled. [49]
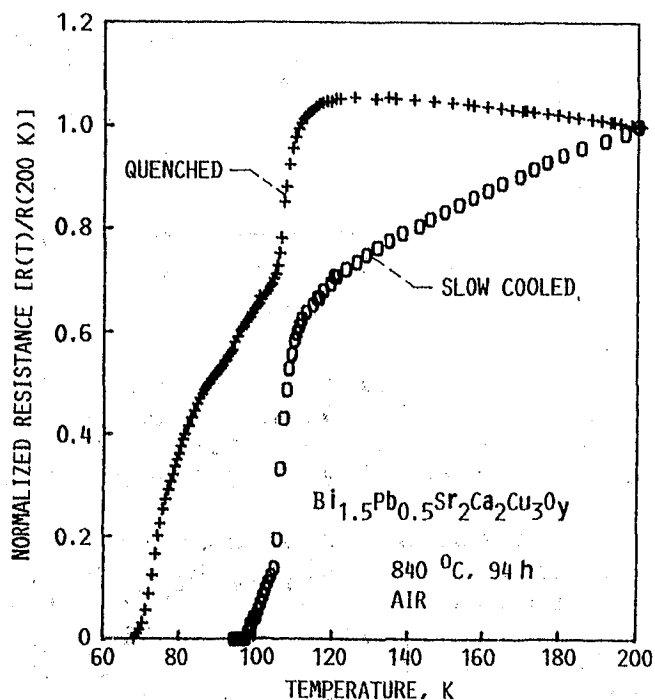

Fig. 29. Effect of cooling rate on the temperature dependence of
electrical resistance of $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ glass
annealed at 840 °C for 94 h in air. [50]

the sample lost weight in N_2. The weight gain in O_2 is probably due to oxidation of Cu(I) to Cu(II) which is necessary for the formation of the 2212 phase.

The influence of cooling rate, after annealing of the $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ glass in air, on the temperature dependence of electrical resistivity is shown [50] in Fig. 29. Two glass samples were annealed for 94 h at 840 °C in air; one was furnace cooled and the other was rapidly quenched to ambient temperature in air. The former sample showed a sharp transition at 110 K with $T_c(R=0)$ of 98 K whereas the latter exhibited a large resistance drop at 110 K with another transition at ~90 K and $T_c(R=0)$ of 68 K. In contrast, for specimens prepared from the glass precursor of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ composition, higher $T_c(R=0)$ was observed [42] in air-quenched samples than those which were furnace cooled after prolonged annealing in air at 840 °C. The reason for these conflicting observations is not clear at this time.
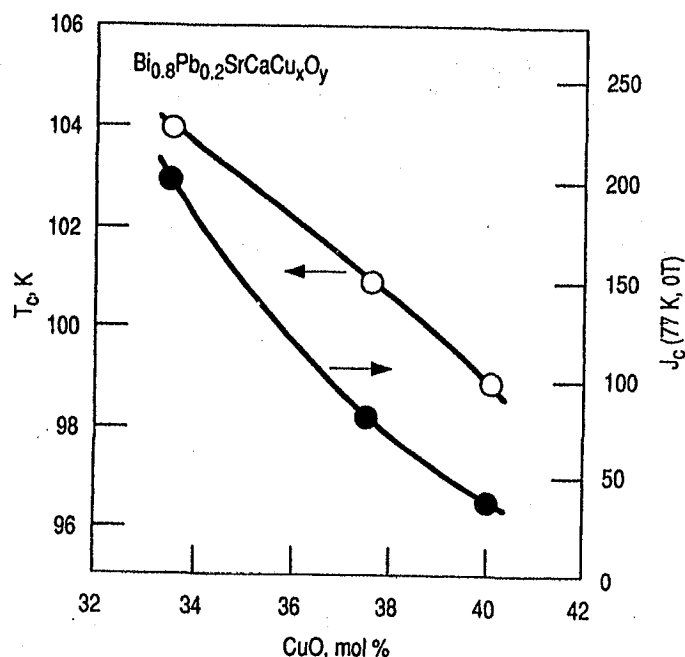

Fig. 30. Values of (O) critical temperature T_c and (●) critical current density J_c (77 K, zero magnetic field) of $Bi_{0.8}Pb_{0.2}SrCaCu_xO_y$ (x = 1.5, 1.8 and 2.0) glass samples annealed at 840 °C for 250 h in air. [69]

Choice of the correct starting composition to prepare the 110 K HTS is very important. The $Bi_{1.84}Pb_{0.34}Sr_2Ca_2Cu_3O_y$ composition results in the formation of the 75 K phase whereas the 110 K phase is mainly produced [83] in $Bi_{1.84}Pb_{0.34}Sr_2Ca_2Cu_4O_y$. However, the excess CuO present as an impurity could result [53, 83,69] in degradation of the superconducting properties such as lower J_c. The use of an excess of CuO or CaO is, therefore, not advisable. High temperature annealing under a proper controlled atmosphere would be more promising. The effect of copper oxide content on the superconducting properties of $Bi_{0.8}Pb_{0.2}SrCaCu_xO_y$

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(x = 1.5, 1.8 and 2.0) glass-ceramics has been investigated [69]. Values of both T_c and J_c (Fig. 30) of samples annealed at 840 °C for 250 h in air decreased with increasing CuO content. The composition with x = 1.5 exhibited the highest T_c(R=0) of 106 K and a J_c of 250 A/cm^2.

The influence of Pb content on the superconductivity of the nominal compositions $BiPb_xSr_2Ca_2Cu_3O_y$, $Bi_{1-x}Pb_xSr_2Ca_2Cu_3O_y$, and $Bi_{1-x}Pb_xSr_2Ca_{3.6}O_y$ has been investigated [85]. Addition of Pb lowered the melting temperature and had a catalytic effect on the formation of the high-T_c phase. The optimum value of x for the highest T_c and the maximum fraction of the high-T_c phase was 0.3. At higher PbO concentration Ca_2PbO_4 formed which assisted in the formation of the low-T_c phase. The optimum value of the Pb content is determined by the competition between the two reactions which result in the formation of the high-T_c phase and Ca_2PbO_4, respectively.

The nearly pure 2223 phase has only been obtained [86-88] by the substitution of lead. The effect of this substitution is not well understood. Lead is known to partially substitute [89] into the bismuth oxide planes of the crystal structure of the 110 K phase. The effect [90] of this substitution is to stabilize the structure and facilitate its formation as a nearly pure phase. Incorporation [91] of PbO lowers the melting point and viscosity of the glass probably by acting as a fluxing agent. However, it has been suggested [91] that a mechanism other than a lowered melting temperature or fluxing action is probably responsible for the beneficial effect of PbO addition. According to Shi et al. [33] the 2212 phase is always formed first because of the higher free energy of the 2223 phase due to the longer c-axis of its unit cell. The kinetics of 2223 phase formation are controlled by calcium and copper diffusion. The presence of lead accelerates growth of the 2223 phase by enhancing diffusion of calcium and copper during insertion of an extra layer of Ca-O and Cu-O into the unit cell of 2212. The Pb atoms are easily incorporated into the structure probably because Bi in the +3 oxidation state and Pb in the +2 state have the same outer electronic shell configuration of $6s^26p^0$. On the other hand, substitution of the bigger Pb^{2+} cation (ionic radius = 1.20Å) for Bi^{3+} (ionic radius = 0.96Å) probably results in the distortion of the crystal lattice.

Nobumasa et al. [92] observed the high-T_c phase directly by high resolution transmission electron microscopy (HRTEM) and found that the Pb atoms were located in the Bi-O layers with an atomic ratio of Pb/Bi ~0.1. More recently the structures and superconducting properties of $Bi_{1-x}Pb_xSrCaCu_{1.5}O_y$ (0 ≤ x ≤ 1) ceramics prepared by the powder sintering method have been examined [93]. For low Pb/Bi ratios, Pb atoms incorporated into the structure of both the low-T_c and high-T_c phases, whereas for high Pb content (x ≥ 0.25) the Pb-rich phase appeared. In light of these results, the value (around x ~ 0.2) of the optimum substitution of Pb for Bi for the formation of the high-T_c phase in $Bi_{1-x}Pb_xSrCaCu_{1.5}O_y$ system might be closely related to the maximum Pb content incorporating in the high-T_c phase. This is in agreement with the results of many other researchers [13,52, 53,69,73] who also found ~20% to be the optimum substitution of Pb for Bi for the formation of a large amount of the high-T_c phase. Ibara et al [61] investigated the effect of doping the

glasses of $Bi_{0.8}Sr_{0.8}CaCu_{1.4}O_y$ and $BiSrCaCu_2O_y$ compositions with various concentrations of PbO. The highest T_c(R=0) of 102 K was observed in $BiPb_{0.1}SrCaCu_2O_y$ annealed in $Ar:O_2 = 12:1$ atmosphere at 840-850 °C for 100 h.

In the Bi-Sr-Ca-Cu-O glass system, the optimum annealing temperature to form the high-T_c phase is ~870 °C. In the presence of PbO this temperature is lowered to ~840 °C. Prolonged firing at 840 °C is very effective [15,50] in enhancing the fraction of the 110 K phase and also in circumventing the intergrain connectivity problem of this phase. However, a $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ sample obtained [15,50] by annealing the glass at 840 °C for more than ten days in air showed T_c(R=0) of 107.2 K, but the sample was still multiphase (Fig. 31) and contained an appreciable fraction of 2212 along with other minor phases. The optimum [13,52,53,69,73,92,93] starting glass composition appears to be $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$. When annealed at ~840-845 °C in air for a long time, a large volume fraction of the 110 K phase is formed in this glass which shows a T_c(R=0) of ~107 K along with a high J_c.

3.6. Bi-HTS DOPED WITH OTHER ELEMENTS

The values of T_g, T_x, and the glass stability factor ($T_x - T_g$) for the Bi-Sr-Ca-Cu-O glasses doped with Al_2O_3 or V_2O_5 are given in Table III. Glassification of the Bi-Sr-Ca-Cu-O system was increased [71,94] by the addition of alumina. Crystallization of a $BiSrCaCu_2Al_{0.5}O_x$ glass rod under a thermal gradient enhanced [95] the growth of the anisotropic plate-like superconducting crystals and improved their intergrain coupling which could result in higher J_c. Also, on crystallization under a thermal gradient the impurity aluminum was excluded [94] from the HTS phases to form alumina fibers. Glass forming ability of $Bi_4Sr_3Ca_3Cu_4O_y$ composition [64] was also enhanced by doping with 0.75 mol % of V_2O_5. The V_2O_5-doped glass also showed higher values of T_g, T_x, and thermal stability than the undoped $Bi_4Sr_3Ca_3Cu_4O_y$ glass. The $(Bi,Pb)_2Sr_2Ca_2Cu_3O_y$ glasses doped with various concentrations of Sb [96], Mo [97], Te [98], or Nb [99], oxides have been prepared by the melt quenching method. The glass-forming ability was retarded by the addition of Nb_2O_5 and TeO_2. In the glass-ceramics obtained by annealing the glasses at different temperatures, formation of the high-T_c superconducting phase was remarkably enhanced by the presence of these oxides. This was due to lowering of the partial melting temperature caused by the coexistence of PbO and the dopant metal oxide.

3.7. FABRICATION OF HTS FIBERS

The glass precursor approach has been used for the fabrication of fibers [64,67,70,72,74,100-103], fine rods [94, 95,104], tapes [83], and thick films [91,105-107] of the Bi-Sr-Ca-Cu-O and Bi-Pb-Sr-Ca-Cu-O systems. Fiber drawing from a glass preform of $Bi_2Sr_2CaCu_2O_y$ composition was not successful [64] due to rapid crystallization. However, continuous glass fibers with diameter of ~100 μm have been successfully drawn [64] of the undoped $Bi_4Sr_3Ca_3Cu_4O_y$ and the one doped with 0.75 mole % V_2O_5 composition by heating the glass preform to 525-550 °C. After 12 h heat treatment at 820 °C, the fibers exhibited a T_c(onset) at 85 K and were still very flexible. Continuous and flexible 120 cm long glass fibers of $Bi_{1.5}SrCaCu_2O_y$ composition
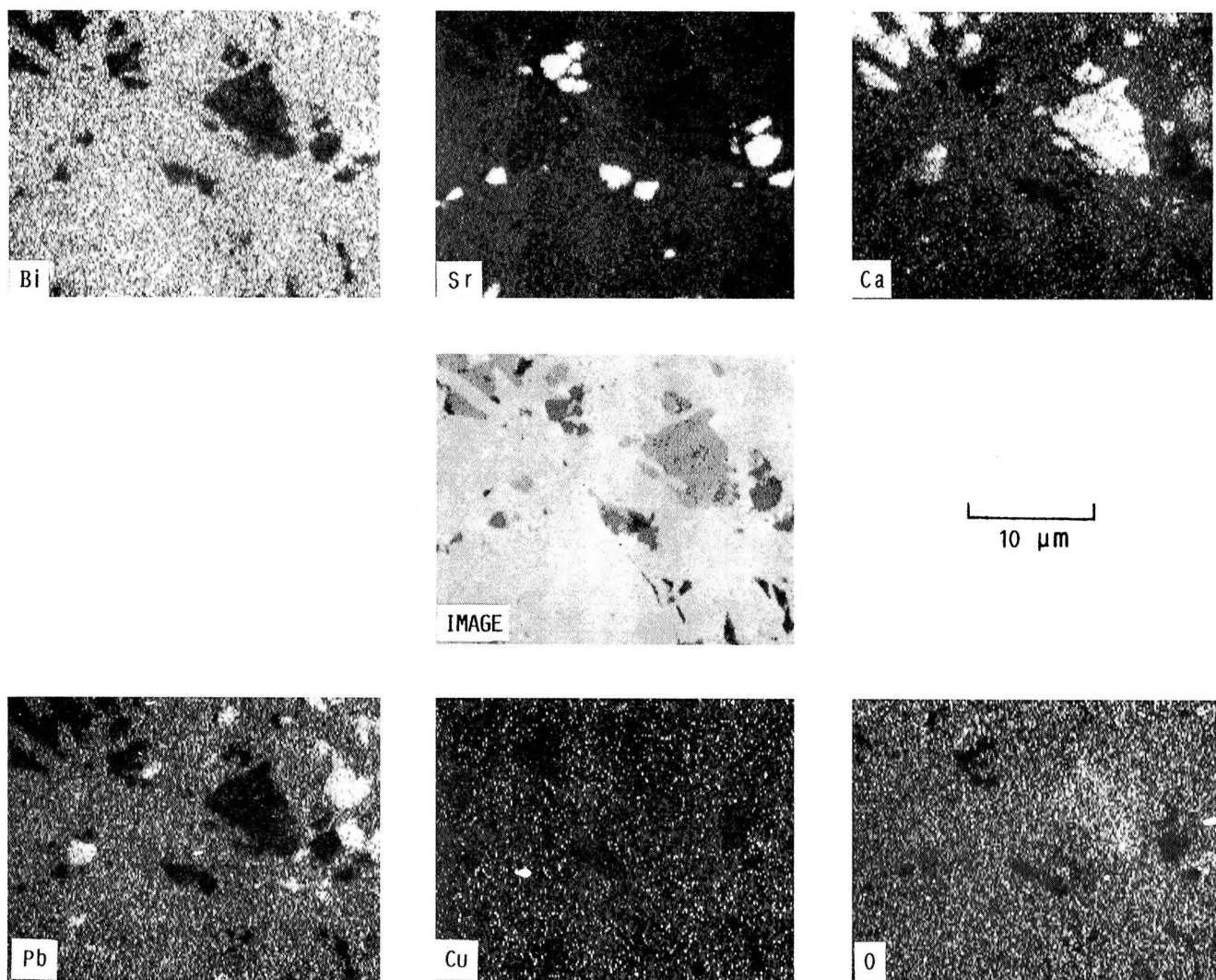
Fig. 31. SEM micrograph and x-ray dot maps of various elements from the polished surface of $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$ glass annealed at 840 °C for 243 h in air and furnace cooled. [50]

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have been drawn [67] from a glass preform at 434 ^{o}C. Glass
fibers of $Bi_2Sr_2CaCu_2O_y$ composition have been drawn [101] from a
glass preform and surface coated with a silver paste. After
annealing at 840 ^{o}C for 5 h in air, the fibers showed a T_c(R=0)
of 70 K and a J_c(60 K) of >40 A/cm^2. Glass fibers of various
compositions in the Bi-Pb-Sr-Ca-Cu-O system have been
prepared [70,103] from melt-quenched glass preforms which became
superconducting after appropriate heat treatments. The glass
ceramic fiber of $Bi_{1.2}Pb_{0.9}Sr_2Ca_2Cu_3O_y$ composition showed a
T_c(R=0) of ⁻109 K and J_c of 1480 A/cm^2 (at 77 K) after 100 h
heat treatment in air at 840 ^{o}C. Glasses with high Bi content in
the $Bi_xPb_ySr_2Ca_2Cu_3O_z$ system were easily drawn [72] into fibers.
After annealing at 840 ^{o}C for 100 h, glass fibers of
$Bi_{2.3}Pb_{0.6}Sr_2Ca_2Cu_3O_z$ composition showed [72] T_c of 84 K.

Preliminary attempts have been made for fabrication [74] of
long slender fibers from melts of $Bi_2Sr_2CaCu_2O_y$ and $BiSrCaCu_2O_y$
compositions using a gas jet fiberization technique. On
subsequent heat treatment at 855 ^{o}C for 16 h in air, the
amorphous fibers were converted into the 2212 HTS. Glass fibers
of short lengths have also been prepared [100] by spinning a
melt of $Bi_4Sr_3Ca_3Cu_4O_y$ composition. On heat treatment at 830 ^{o}C
for 24 h, the glass fibers crystallized into the 2212 phase
along with small amounts of $Bi_2Sr_2CuO_8$ and CuO phases and showed
a T_c(onset) of ⁻80 K.

The glass precursor technique has also been employed [108]
to apply a superconducting coating on a Pt wire by passing it
through a melt of 2212 composition at 1075 ^{o}C followed by
quenching. On subsequent heat treatment at 800 ^{o}C, the
superconducting 2212 phase is formed by devitrification of the
glassy coating. The composite wire showed a T_c(R=0) of ⁻60 K and
could be flexed and wound without effecting its superconducting
behavior.

4. Tl-Ba-Ca-Cu-O SYSTEM

Nassau *et al* [9] tried to prepare glasses of the
compositions $Tl_2Ba_2CaCu_2O_x$, $Tl_2Ba_2Ca_2Cu_3O_x$, and the latter
containing lead by melting 5 g batches of the powder in an
iridium crucible in air for less than 3 minutes. Considerable
loss of Tl_2O occurred during melting as indicated by black
smoke. The melt was rapidly quenched between twin metal rollers
attaining a quenching rate of ⁻10^7 K/s. Some glass was obtained
only for the $Tl_2Ba_2CaCu_2O_x$ composition. On heating, this showed
a T_g of 280 ^{o}C and a number of exotherms starting at 300 ^{o}C. In
the XRD patterns of the heat treated glass, strongest
diffraction peaks of CuO, Cu_2O, and possibly $CaCu_2O_3$ were
present alongwith a number of other peaks which could not be
indexed. The study was not pursued any further.

5. Y-Ba-Cu-O SYSTEM

Rapid quenching of small droplets of $YBa_2Cu_3O_x$ melt on steel
plates resulted [109] in an amorphous material which showed T_g
of 330 ^{o}C and T_x of 780 ^{o}C in the DTA along with a large number
of endothermic peaks which were not explained. In the view of
the present reviewer, the reported values of T_g and T_x are
doubtful. The orthorhombic $YBa_2Cu_3O_{7-\delta}$ HTS phase was formed on
heat treatment for 12 h in flowing O_2 at 850 ^{o}C, but some other
phases were also present. On annealing in flowing O_2 for 12 h at

950 °C, almost phase pure HTS material was produced with a $T_c(R=0)$ of ˜92 K. Attempts by many other researchers [110-121] did not result in the formation of a glassy material on rapid cooling of the R-Ba-Cu-O (R = Y, Gd, Yb) melts. Even rapid quenching of Y-Ba-Cu-O melt using a metal twin-roller did not form glass. The presence of a glass former [122-124] such as B_2O_3 was helpful in obtaining this composition in the glassy state. However, the HTS phase formed on heat treatment of this glass was discontinuous.

6. SUMMARY AND CONCLUSIONS

It is very difficult to form the Y-Ba-Cu-O and the Tl-Ba-Ca-Cu-O HTS systems in the glassy state by rapid quenching of the melts. The Bi-HTS systems can, however, be obtained as glasses from fast melt quenching. Bi_2O_3 acts as the glass former and plays an important role. The thermal stability factor, $T_x - T_g$, is large for glasses rich in Bi_2O_3 and alkaline earth oxides whereas the CuO-rich glasses show smaller values.

Superconducting material having high T_c and J_c and containing a large volume fraction of the 110 K phase can be formed from a $Bi_{0.8}Pb_{0.2}SrCaCu_{1.5}O_y$ glass by annealing at ˜840 - 845 °C in air for an extended period of time followed by slow cooling. However, synthesis of a single phase 2223 HTS material by the glass precursor approach appears to be difficult. The advantage of the starting components being intimately mixed in the melt is lost as the 2223 phase does not precipitate out directly from the glass matrix but is preceded by the crystallization of other phases. The high-T_c phase is produced at high temperatures by a slow diffusion controlled reaction between the phases formed at lower temperatures.

Continuous Bi-Sr-Ca-Cu-O or lead-doped glass fibers can be drawn by heating a glass preform around its softening point. However, the sluggish kinetics of high-T_c phase formation presently offers a severe limitation on the practical utility of the glass precursor approach to Bi- HTS fabrication, particularly for continuous fiber or wire.

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13. ABSTRACT (Maximum 200 words)

The available studies on the synthesis of high–T_c superconductors (HTS) via the glass precursor approach have been reviewed. Melts of the Bi-Sr-Ca-Cu-O system as well as those doped with oxides of some other elements (Pb, Al, V, Te, Nb, etc.) could be quenched into glasses which, on further heat treatments under appropriate conditions, crystallized into the superconducting phase (s). The nature of the HTS phase (s) formed depends on the annealing temperature, time, atmosphere and the cooling rate and also on the glass composition. Long term annealing was needed to obtain a large fraction of the 110 K phase. The high-T_c phase did not crystallize out directly from the glass matrix, but was preceded by the precipitation of other phases. The 110 K HTS was produced at high temperatures by reaction between the phases formed at lower temperatures resulting in multiphase material. The presence of a glass former such as B_2O_3 was necessary for the Y-Ba-Cu-O melt to form a glass on fast cooling. A discontinuous $YBa_2Cu_3O_{7-\delta}$ HTS phase crystallized out on heat treatment of this glass. Attempts to prepare Tl-Ba-Ca-Cu-O system in the glassy state were not successful.

14. SUBJECT TERMS

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